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Report

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CPEA 28: Airborne Particulate Concentrations and Numbers in the United Kingdom (phase 2)

Annual Report - 2006

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Approved on behalf of Managing Director, NPL
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Annual Report for 2006 on the UK Airborne Particulate Concentrations and Numbers Network

Executive Summary

This Report was prepared by NPL as part of the 2005-2007 UK Airborne Particulate Concentrations and Numbers contract with the Department for the Environment, Food and Rural Affairs. This is the Annual Summary Report for 2006 and contains:

- Summary of Network Operation and QA/QC procedures
- Data capture per instrument per month
- A graphical presentation of all validated and ratified network data from 2006
- Comparison of 2006 particle numbers and concentrations of sulphate, nitrate and carbon with levels in recent years.
- Policy update on relevant areas
- Update of research and equipment in the field

The operation of the network in 2006 was structured in the same way as the previous year, with King's College London responsible for data collection and NPL performing QA/QC activities. The network consists of 23 instruments at ten sites across the UK. The instruments include automatic elemental and organic carbon analysers, automatic nitrate analysers, particle counters, particle sizers, filter samplers for daily nitrate, sulphate and chloride, and meteorological equipment.

In the interests of continual improvement of the network, some additional work was undertaken during the course of the year. Comparison studies have been carried out and recommendations have been made regarding:

1. Alternative laptops for the particle counting instruments
2. Two commercially available SMPS systems
3. Best practice for manual and automatic organic and elemental carbon methods

Data capture during 2006 was variable. The Thermo 5400 automatic carbon, and the Thermo 8400N automatic nitrate were both discontinued by the manufacturer early in 2007. Despite routine maintenance and regular visits from the Equipment Support Unit, these instruments tended to have lower data capture than the 80% target, with an annual average of 66% for carbon and 71% for nitrate. The Partisols (nitrate, sulphate and chloride), CPCs and meteorological instruments have data capture rates above 90%.

The SMPS systems in place at the beginning of the year (TSI model 3071) were not operated after March 2006, as the manufacturer no longer supported them. They were replaced by the current TSI model 3936L75 in March 2007, in agreement with Defra.

Yearly averages have been calculated and compared with those from recent years. At most sites, particle numbers have increased, and there is also a corresponding increase in the concentration of sulphate and chloride.

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Introduction

This Report was prepared by NPL as part of the 2005-2007 UK Airborne Particulate Concentrations and Numbers contract (CPEA 28) with the Department for the Environment, Food and Rural Affairs.

This is the Annual Summary Report for the UK Airborne Particulate Concentrations and Numbers Network for 2006 and contains:

- Summary of Network Operation and QA/QC procedures
- Data capture per instrument per month
- Graphical presentation of all validated and ratified network data from 2006
- Comparison of 2006 particle numbers and concentrations of sulphate, nitrate and carbon with levels in recent years
- Policy update on relevant areas
- Update of research and equipment in the field

Network Operation

Overview

The operation of the network in 2006 was structured in the same way as the previous year. King's College London (KCL) has continued in its role as the Central Management and Control Unit (CMCU). It has carried out activities including routine collection of data from site, initial data validation and instrument fault finding, routine liaison with the Local Site Operators (LSO) and the Equipment Support Unit (ESU). The QA/QC activities were performed by NPL and included site audits, instrument calibrations, inter-laboratory performance schemes and data ratification.

In 2005, NPL published a Strategic Network Review[i], outlining experts' opinions on important topics for future research within the scope of this network, and recommending long-term changes in order to achieve this. A set of interim proposals was discussed with Defra in April 2006, and some changes were agreed, relating to the SMPS and automatic carbon analysers.

Improvements to Network Operation

Following several changes to the network operation that were introduced in 2005 (described in the 2005 Annual Report[ii]), NPL and KCL have continued to make improvements to ensure high data capture rates and data accuracy.

Replacement Computers for CPC and SMPS Analysers

During 2005 some CPC and SMPS data was lost due to problems with the laptop computers. Standard laptops are not designed for continuous use, or for use in non-office conditions. At some sites, lack of air conditioning, a damp environment, vibrations caused by other instruments and aging computers were considered to be contributing factors to these breakdowns. In August 2006 two new types of site computer were tested at Marylebone Road. These were:

- Shoebox Small Form Factor PC (a compact version of a standard desktop computer, believed to be more robust than a laptop).
- Rough Rider Junior (a rugged laptop, designed for use in extreme conditions).

Both types performed well during a six-month test period and are being installed at sites, depending on the available space.

New SMPS Analysers

In March 2006, the operation of the three old SMPSs (TSI model 3071) ceased, following discussions with Defra. Each instrument had developed serious problems and was no longer supported by the manufacturer (TSI Instruments). During September and October 2006, NPL carried out an intercomparison of two commercially available SMPS analysers, with the aim of recommending one model to replace the three old network analysers at Marylebone Road, Harwell and Bloomsbury. In light of the scientific and operational differences of the two analysers, the price and desirability of providing results that can be compared to historic data, the TSI analyser (model 3936L75) was judged to be most suitable for the network. The new systems were installed at the three sites in March 2007.

Harwell LSO Change

On 1st December 2006, Birmingham University took over the local site operational duties at Harwell. The University has considerable experience in operating the network instruments and has offered to temporarily install their SMPS at the site if required.

Automatic Carbon Analysers

In July 2006 the Belfast instrument was returned to the 3-hour sampling mode as the low concentrations measured at this site were close to the limit of detection.

Harwell Site Move

Equipment from this network was moved from buildings B573.2 and B573.T2 to B585, which is approximately 100m east of the original monitoring stations. Air Monitors, the Equipment Support Unit, moved the automatic carbon, automatic nitrate and Partisol analysers on 21 February 2006. Netcen installed the SMPS in the new building on 23 February 2006. The meteorological mast was moved on 18 March 2006 and realigned under the instruction of Netcen. To ensure the safety of site visitors, mobile steps were installed in 2006 to provide access to the roof of B585.

Automatic Nitrate Analysers

It has been highlighted in previous audit reports that the molybdenum converters in the 8400N automatic nitrate analysers have a low efficiency. Four new converters have been purchased and two have been installed - into the instrument at Belfast and into the spare instrument. The new parts will also be fitted at Harwell and Marylebone Road.

Instrumentation

A list of network instruments can be found in Annex 1. Annex 2 contains a map showing the locations of the deployed instruments. More detailed descriptions of the theory of operation, calibration and the estimated uncertainty in the results are included in the recent NPL measurement uncertainty report.[iii] A summary of the report is presented in Annex 3.

Particle Counting and Sizing Analysers

These instruments operate on the principle of passing the sample through clean air supersaturated with butanol, causing a butanol droplet to form around each particle so that they can be counted optically. In a CPC, total number concentrations of particles in the size range ~7nm to several microns are determined in this way, either by individual number counting (at low concentrations) or using an optical integrating method (at high concentrations). In the case of an SMPS, the sample entering the CPC has passed through air ionised by a radioactive device (based on Krypton-85) that gives an electric charge to a known fraction of the particles, and then through a controlled electrical potential that separates the charged particles according to their electrical mobility.

Automated Nitrate and Carbon Analysers

Both systems operate on broadly similar principles. For the nitrate analyser the particulate content of the air is sampled onto a flash strip via an internal cyclone inlet. For the carbon analyser the particulate content of the air is sampled through a size selective inlet and then collected by an impactor. In the case of the nitrate analysers, the system flash heats the particulate matter and the quantity of NO_x produced is analysed, and in the case of the carbon analysers, CO_2 is produced. In the latter case the combustion is initially performed at a temperature of 320ºC to 370ºC to determine the organic carbon content and subsequently at a temperature of 650ºC to 700ºC to determine the elemental or 'soot' carbon content.

Partisol 2025

Particulate samples from air that has passed through a size-selective inlet are collected on an Emfab (PTFE-bound glass fibre) filter. Partisols provide daily particulate samples that are analysed in the laboratory by ion chromatography, for sulphate, nitrate and chloride content.

Additional Work

NPL has undertaken two short research projects in 2006, with funding from this network.

SMPS Intercomparison

A comparison of new SMPS systems was carried out to evaluate their suitability for deployment as field instruments. Two commercially available instruments were tested, from the two main manufacturers - TSI Instruments (model 3936L75) and Grimm Aerosol (SMPS+C). The instruments were tested in both the laboratory and in the field, in September to October 2006.

The data showed that both instruments agreed broadly, but in the short period available before a choice had to be made, the TSI system demonstrated more reliable behaviour in unattended operation, and was chosen to replace the network instruments.

Organic and Elemental Carbon

Parallel measurements of the organic and elemental carbon (OC/EC) content of PM_{10} suspended particulate matter were undertaken at Marylebone Road during the period 07/09/06 to 31/12/06. Measurements were made manually using a Partisol sampler (containing quartz filters) with a Sunset Laboratory Carbon Aerosol Analysis instrument at NPL, and with the automatic Thermo Series 5400 ambient carbon analyser. The results and implications of this study were published by NPL in February 2007.[iv] A summary of the report is presented in Annex 4.

The intercomparison showed that the manual method reported organic carbon concentrations that were similar to the automatic method, while it reported elemental carbon concentrations between three and four times the magnitude of the automatic method. A US EPA study[v] in December 2005 also showed that the automatic method gave similarly poor agreement with the manual reference method for elemental carbon. The manual method reported total carbon (OC and EC) about twice as high as the automatic method.

The results are interpreted as a serious underestimate of EC by the Thermo 5400 automatic analyser, possibly due to much of the elemental carbon not being collected by the impactor and passing through the analyser undetected.

Further work is to be carried out at an urban background site to determine whether these results are applicable to other site locations in the UK.

Data Quality

The summary of quality assurance and quality control procedures used during the measurement and ratification process are listed below:

- Continued training of, and regular communication with, Local Site Operators (LSOs)
- The KCL Duty Officer is available to advise LSOs 365 days per year
- Data collection is automated by the MONNET system at KCL
- Automatic and manual data validation is followed by rigorous ratification procedures
- Scheduled instrument services and calibrations are ongoing
- An annual audit of all sites and instruments has been conducted by NPL, and the results were published in July 2006[vi]
- Calibration data produced at audit by the ESU, and regular calibrations carried out automatically or by the LSOs, are all used to produce an appropriate scaling factor to apply to the data
- Routine maintenance is carried out on all instruments according to manufacturers' instructions
- The Thermo 5400 carbon and 8400N nitrate analysers are calibrated with CO_2 and NO, which are certified at NPL and are traceable to primary standards
- The Equipment Support Unit (ESU) is contracted to respond to breakdowns within 48 hours
- Research into particulate mass, chemical composition and speciation continues at NPL under the DTI's Valid Analytical Measurement programme.

Scheduled Instrument Services and Calibrations

Since June 2005, CPCs have been serviced and calibrated annually, as recommended by the manufacturer (TSI Instruments) and detailed in Table 1. The instrument response is measured before and after the service to allow data to be corrected during ratification.

Site	05/06 service	06/07 service
Belfast	16/02/06	24/02/07
Birmingham	21/07/05	11/08/06
Glasgow	17/11/05	24/11/06
North Kensington	24/04/06	26/03/07
Marylebone Road	15/09/05	17/10/06
Manchester	10/10/05	03/11/06
Port Talbot	10/08/05	20/09/06

Table 1. Annual CPC service and calibration dates

The automatic nitrate and carbon analysers, and the Partisols are serviced twice yearly by the ESU, Air Monitors. The service procedure includes replacing old or worn parts, calibration of NOx analyser and CO_2 sensor, temperature and flow calibrations, leak tests and pump refurbishment. The services completed during 2006 are indicated in Table 2:

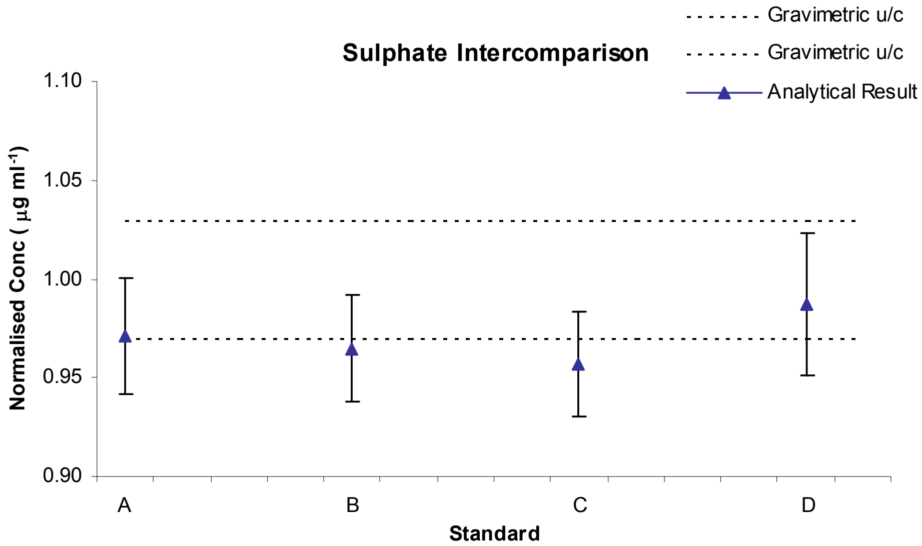
Site	Instruments	Service 1	Service 2
Belfast	Partisol Carbon Nitrate	17/05/06	03/10/06
Harwell	Partisol Carbon Nitrate	23/05/06	06/10/06
Marylebone Road	Partisol Carbon Nitrate	10/05/06	02/11/06
North Kensington	Partisol Carbon	25/05/06	28/09/06

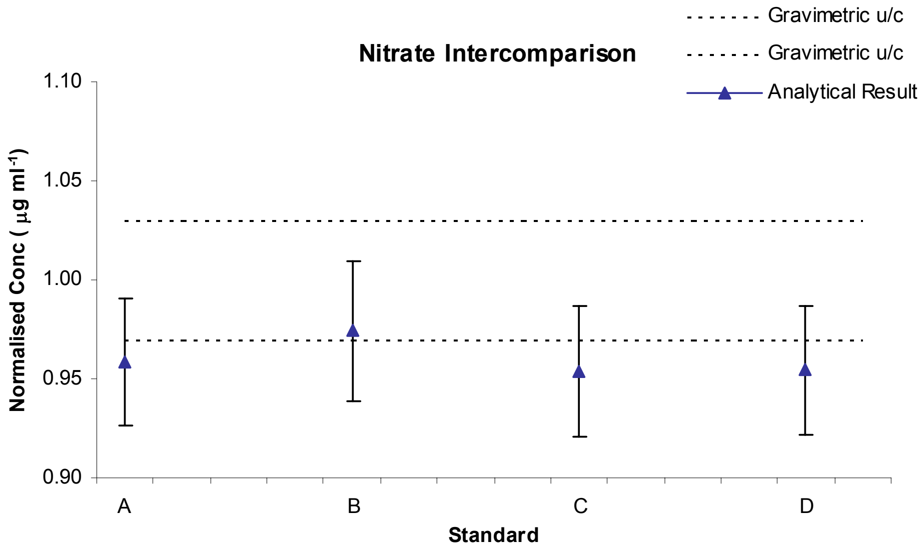
Table 2. Equipment services completed during 2006 - for Partisol, 5400 carbon and 8400N nitrate analysers

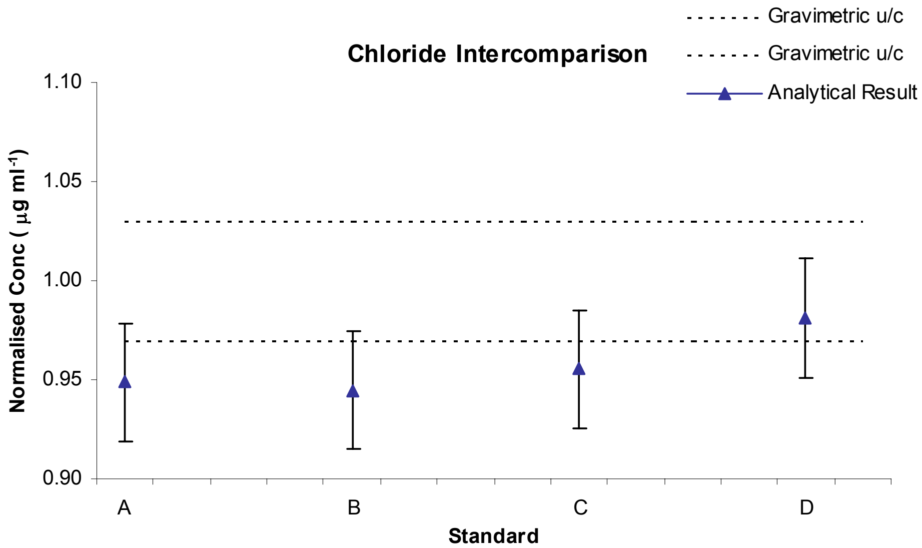
Anions on Filters Intercomparison

Analysis of the daily Partisol filters for nitrate, sulphate and chloride is currently performed by King's College London by ion chromatography. To ensure the quality of the data produced, an intercomparison with NPL is carried out annually.

In July 2006, NPL gravimetrically prepared four standard solutions, each containing a different concentration of each anion (in the range expected from the network). An aliquot of each solution was analysed by KCL using its standard operating procedure. The results for each anion are shown in the graphs below. Each result agrees with the gravimetric value within the uncertainty of the measurement at the 95% level of confidence.







Figures 1 to 3 Results of the ion chromatography intercomparison between NPL and King's College London

Network data

Data Capture

Overall data capture rates for each instrument type in 2006 are given in Table 3, and are compared with 2005 data capture. Data capture is calculated as hours of ratified data as a percentage of available hours (unless otherwise stated). Instrument down times due to scheduled maintenance and calibration are not included in the calculation of data capture, in line with relevant European Air Quality Directives.

Instrument Type	Number of Network Instruments	Data Capture 2006	Data Capture 2005	Data Capture 2005 (NPL operation)
Automatic Carbon	4	66%	29%	63%
Automatic Nitrate	3	71%	89%	87%
Partisol (daily)	4	93%	80%	85%
CPC	7	91%	67%	84%
Meteorological data	2	99%	92%	92%

Table 3. Data Capture across the Airborne Particulate Network during 2005 and 2006.

The data capture for the SMPSs is not included in this table, as the instruments were withdrawn from the network in March 2006. This decision was made in agreement with Defra and a study of alternative instruments was carried out, as detailed on page 10 of this report.

These data capture rates are an improvement on those achieved during 2005, for automatic carbon, Partisol, CPC and meteorological instruments.

Instrument Performance And Concentration Data

The following sections discuss each instrument type. There is a monthly breakdown of data capture at each site along with reasons for data loss. The concentration data from each instrument is also presented in a graphical format and unusual or interesting occurrences are noted and discussed.

Full, validated data from 2006 will be used to form the basis of future topic reports, produced in collaboration with Birmingham University.

Automatic Carbon Analysers

Monthly data capture rates for the automatic carbon instruments during 2006 are displayed in the table below:

Site	Belfast	Harwell	North Kensington	Marylebone Road
January	0%	96%	59%	92%
February	42%	81%	14%	89%
March	41%	69%	29%	34%
April	0%	75%	67%	0%
May	39%*	4%*	78%*	62%*
June	87%	45%	36%	93%
July	85%	91%	99%	86%
August	93%	91%	96%	53%
September	95%	94%	100%*	93%
October	10%*	38%*	99%	100%
November	25%	0%	99%	100%*
December	19%	0%	99%	93%
Average	**45%**	**57%**	**74%**	**75%**

* Month in which service was performed

Table 4. Monthly data capture for Carbon instruments during 2006.

The Equipment Support Unit carries out services and instrument calibrations twice a year. One day has been allowed for each of these service visits and that is reflected in the data capture calculation. An 'available' day has been removed from Harwell during February to account for the site move.

Historically, the Thermo 5400 carbon instruments have a poor record of data capture and data quality, due to frequent technical failures and calibration difficulties. The 2005 EPA study[5] showed that these instruments do not agree with the manual reference method, especially for elemental carbon, and this has been confirmed by NPL's recent comparison at Marylebone Road[4]. The 5400 carbon has now been discontinued by the manufacturer and will not be supported past March 2008.

For these reasons, the data is presented as validated only. ***This data is not ratified***. The data is shown on the following pages:

Belfast

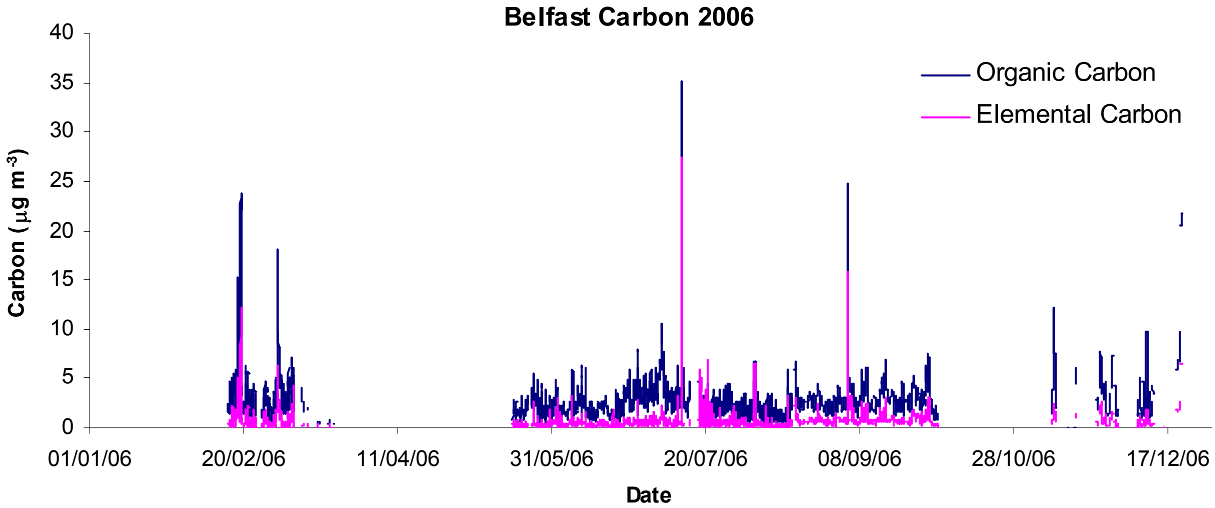


Figure 4a. Organic and elemental carbon concentrations at Belfast in 2006

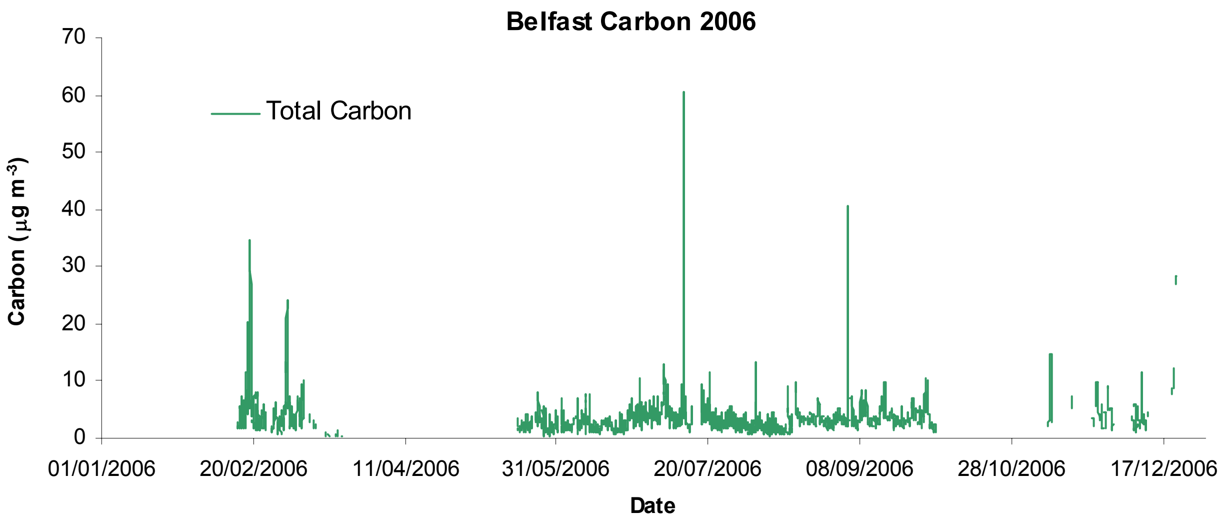
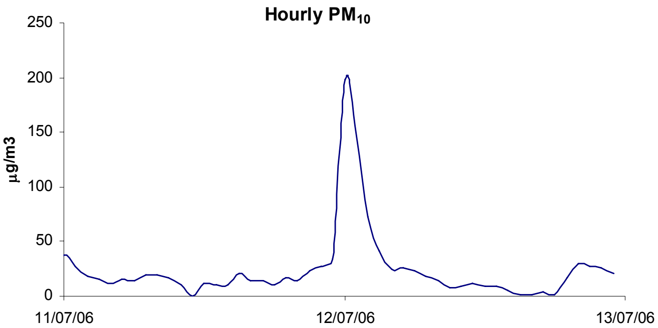


Figure 4b. Total carbon concentrations at Belfast in 2006

During January and some of February, the Belfast instrument was turned off following a fault, waiting for a new CO_2 optical sensor and central processing unit. Unfortunately, it was only operational for a few weeks before another fault occurred and additional parts were required from the manufacturer. It has become increasingly difficult to source parts for the automatic carbon analysers, causing delays in repair work. In October a pump malfunction meant that the instrument was again turned off for a few weeks. Sporadic time coverage in the last two months of the year was caused by an electrical problem at the site, where the instrument was turned off every time the cabin lights were turned on, requiring the instrument to be reset by the LSO. It was not possible to do this remotely.

A significant spike was seen between 22:00 on 11/07/06 and 02:00 on 12/07/06, which is also reflected in the PM_{10} data, as shown in Figure 4c. The LSO has confirmed that this was due to the traditional bonfires lit to commemorate the Battle of the Boyne.



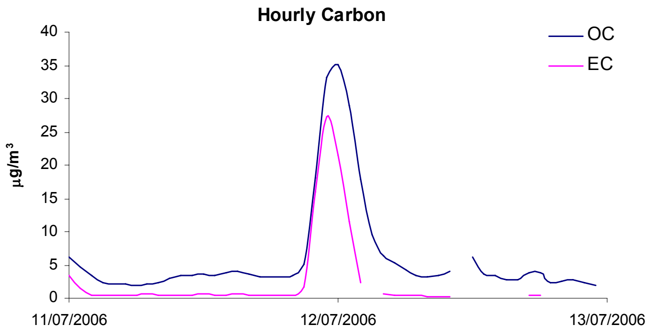


Figure 4c. Belfast hourly PM_{10} data spike in July 2006

A second spike is seen in the automatic carbon data on 03/09/06. There is no correlating PM_{10} peak, although data is incomplete during early September.

Harwell

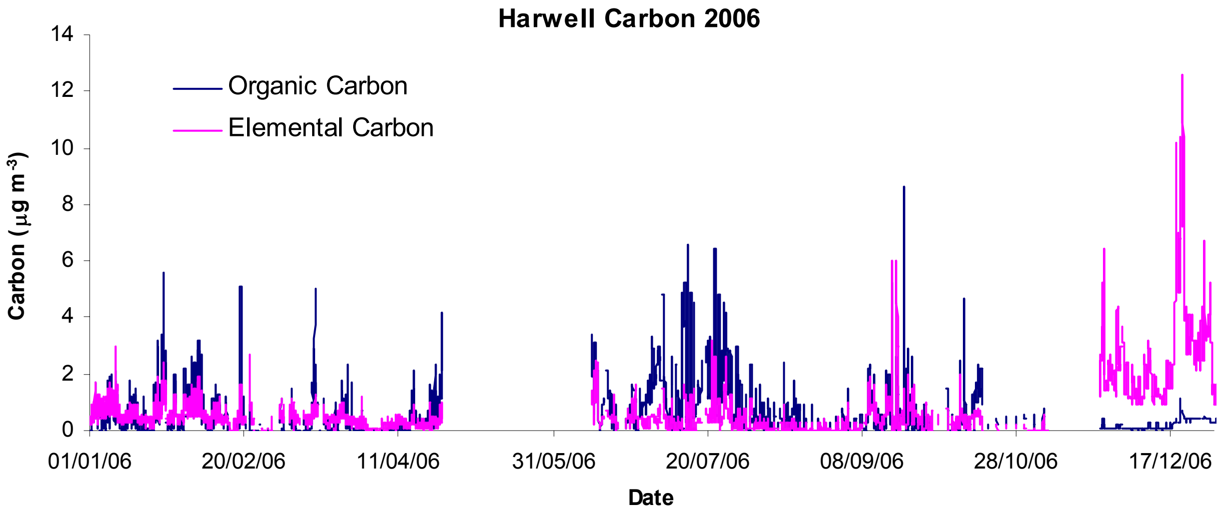


Figure 4d. Organic and elemental carbon concentrations at Harwell in 2006

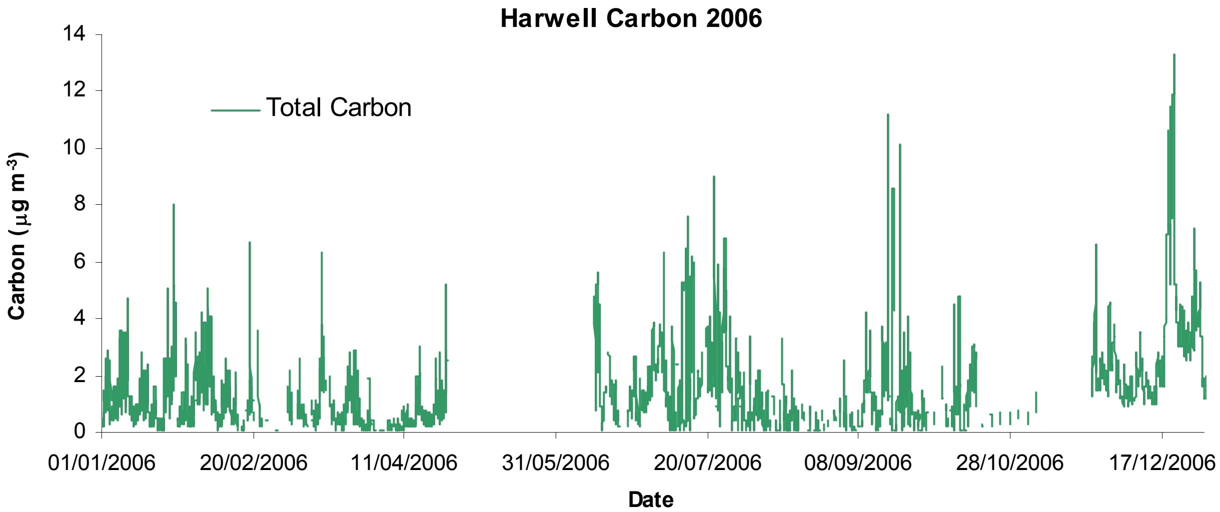


Figure 4e. Total carbon concentrations at Harwell in 2006

During May and June a software fault meant that the Harwell instrument was stuck in 'clean' mode and would only run one sample before stopping automatically. Despite several visits from the LSO and Equipment Support Unit, this issue was not resolved until 13/06/06. This same problem was also experienced in November.

During December it can be seen that the ratio of organic to elemental carbon changes significantly. This behaviour has been identified in data produced by the 5400 instruments several times during the last few years. It is not limited to one instrument or one site. This data cannot be fully ratified, and although it is anomalous, this example has not been removed from the dataset.

Marylebone Road

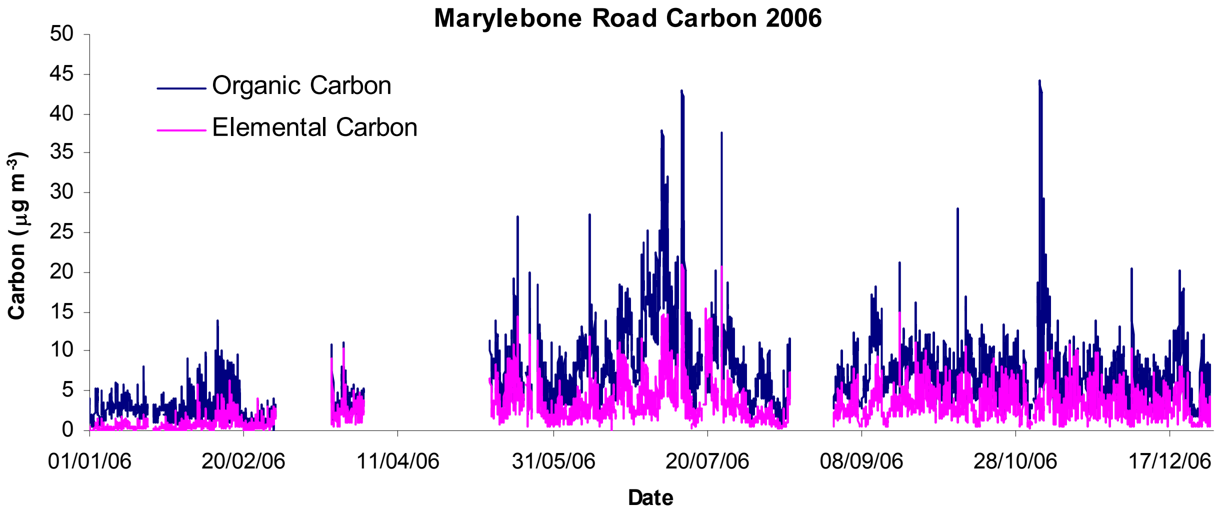


Figure 4f. Organic and elemental carbon concentrations at Marylebone Road in 2006

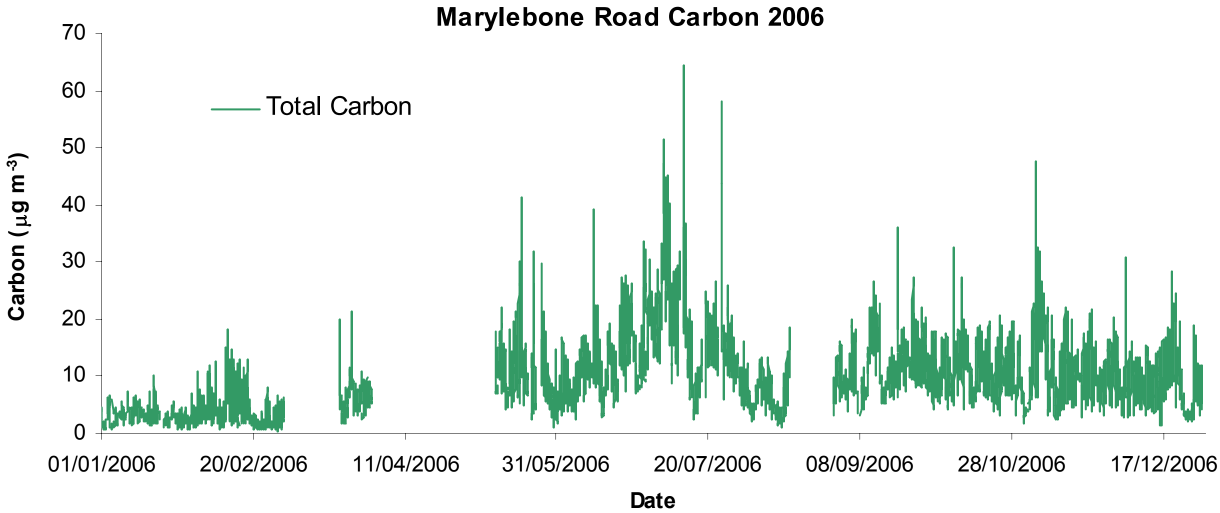


Figure 4g. Total carbon concentrations at Marylebone Road in 2006

Due to unavailability of parts, the instrument was switched off for several weeks in April and May. The LICOR CO_2 analyser on the control board was replaced at the end of August, significantly improving data capture towards the end of the year. The large spike of organic carbon in November corresponds to the Guy Fawkes / bonfire night celebrations. A similar peak was also recorded at North Kensington.

A study was recently undertaken at Marylebone Road, with a co-located Partisol and the network automatic carbon analyser. The Partisol filters were analysed for organic and elemental carbon by a Sunset Laboratory carbon aerosol analysis laboratory instrument. The results from the 'manual' method showed that the elemental carbon concentration is usually higher than the organic. This is not in agreement with the data produced by the automatic carbon analyser.

North Kensington

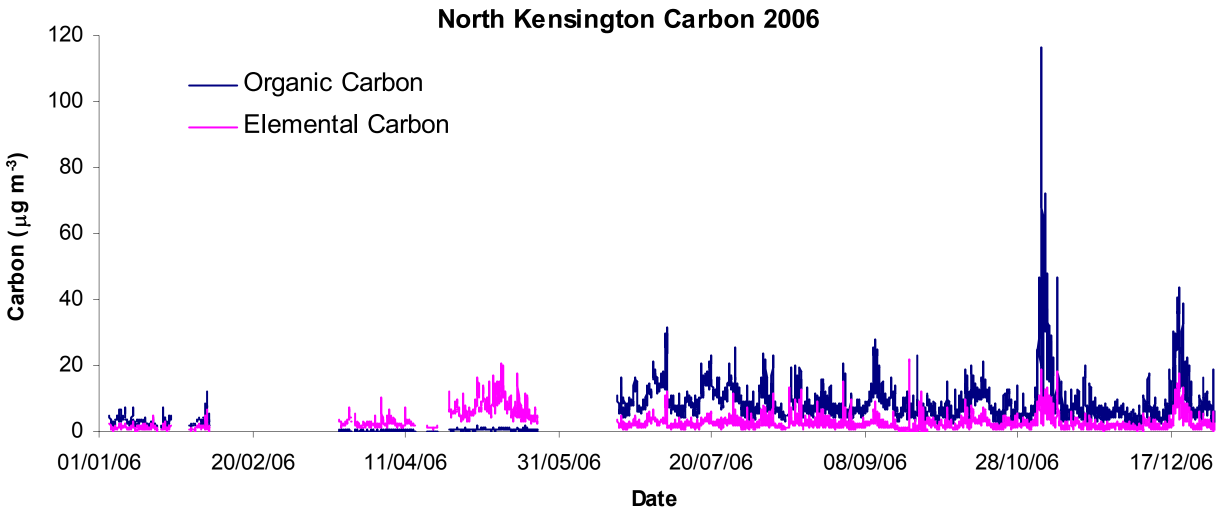


Figure 4h. Organic and elemental carbon at North Kensington 2006

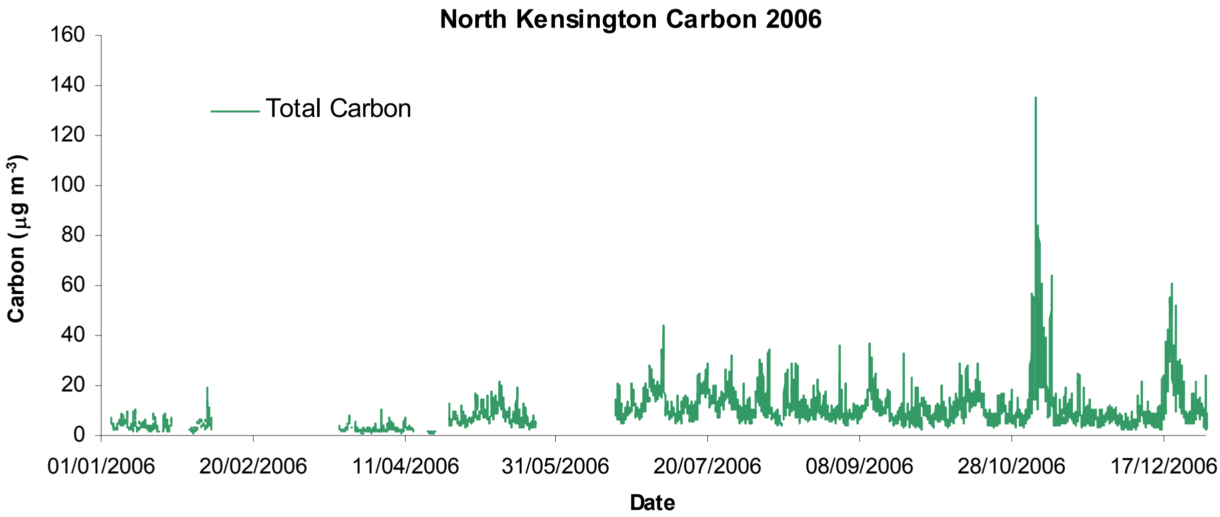


Figure 4i. Total carbon concentrations at North Kensington 2006

Instrument faults during February and March led to the spare 5400 being installed at North Kensington on 20/03/06. This replacement instrument, however, did not produce data consistent with that seen previously at this site. This is believed to be due to a similar problem as seen at Harwell in December. Again, as the data cannot be fully ratified, this example has not been removed. The original analyser was reinstalled at the beginning of June following repair, and the data capture for the second half of the year reached 99%.

The large spike of organic carbon in November corresponds to the Guy Fawkes / bonfire night celebrations and a similar peak was also seen at Marylebone Road. Elevated levels of carbon were recorded at all sites during the period 17/12/06 to 24/12/06 due to the foggy, still weather conditions in the UK at that time. Similar peaks are also seen in heavy metals, black smoke and PM_{10} data.

Further analysis of the carbon data is not considered to be appropriate in this Report.

Automatic Nitrate Analysers

Monthly data capture rates for the automatic nitrate instruments during 2006 are displayed in the table below:

Site	Belfast	Harwell	Marylebone Road
January	57%	64%	99%
February	99%	72%	95%
March	91%	37%	40%
April	0%	99%	87%
May	3%*	91%*	63%*
June	62%	58%	85%
July	37%	43%	75%
August	99%	83%	39%
September	89%	56%	52%
October	100%*	72%*	94%
November	100%	78%	61%*
December	99%	73%	91%
Average	**70%**	**69%**	**73%**

* Month in which service was performed

Table 5. Monthly data capture for automatic nitrate instruments during 2006.

The Equipment Support Unit carries out services and instrument calibrations twice a year. One day has been allowed for each of these service visits and that is reflected in the data capture calculation. An 'available' day has been removed from Harwell during February to account for the site move.

Graphs of the nitrate concentrations measured at each site are shown on the following page:

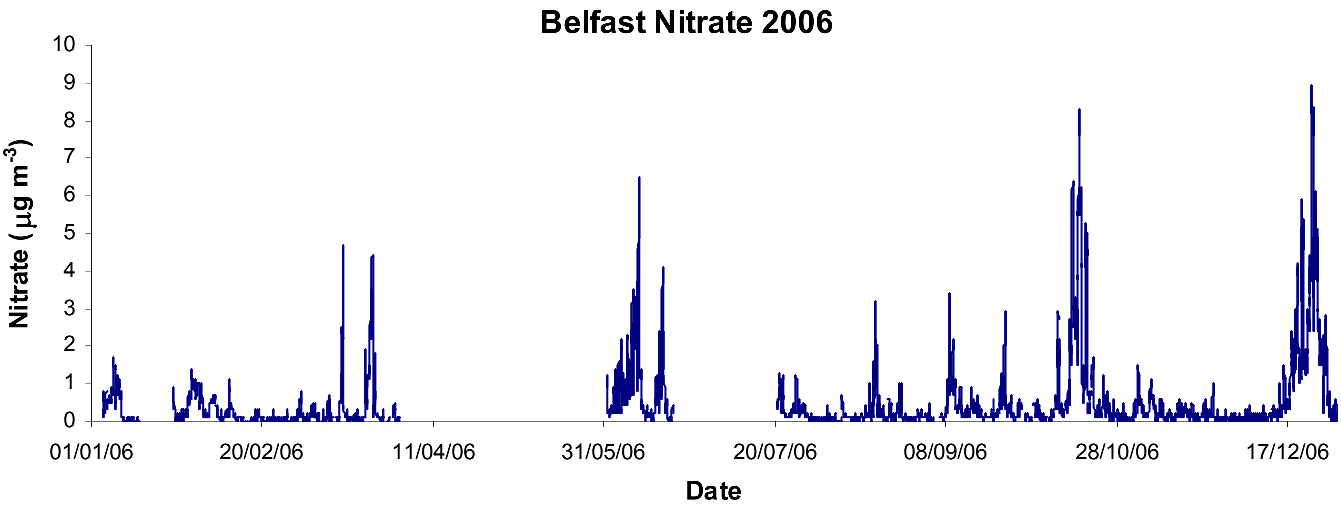


Figure 5a. Nitrate concentrations at Belfast in 2006

As a result of a sample pressure fault in April and May, the Belfast analyser was reporting zero concentrations for prolonged periods. These were removed during ratification. Some data was also lost in June and July when the analyser was switched off due to the dehumidifier being broken.

The peak occurring between the 16th and 20th October is also recorded in the Belfast daily nitrate (Partisol) results.

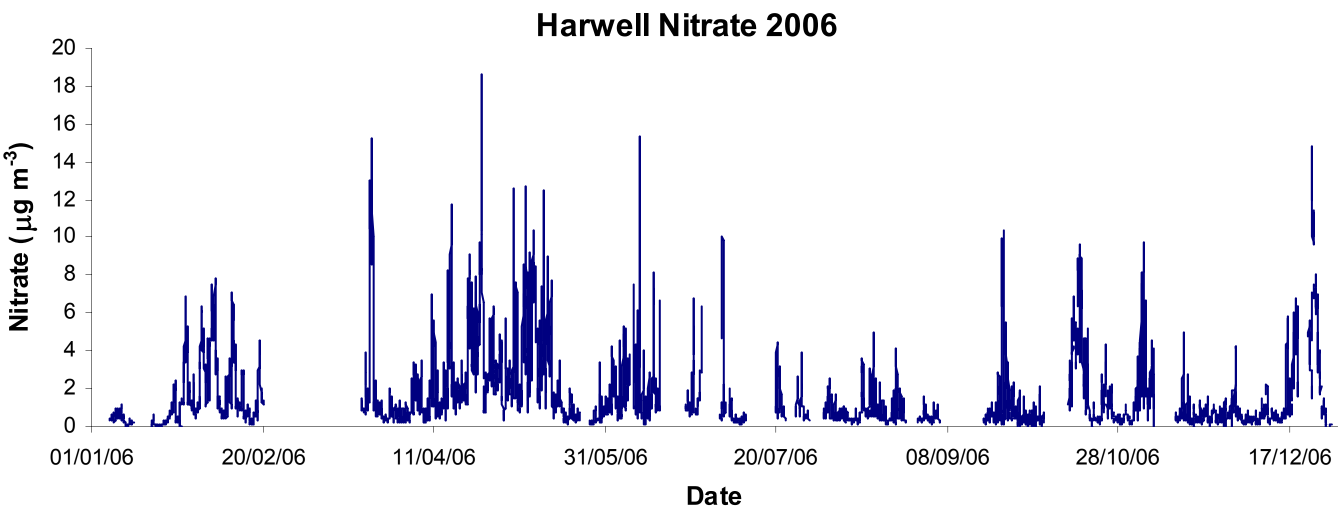


Figure 5b. Nitrate concentrations at Harwell in 2006

On 21/02/06 the nitrate analyser at Harwell was removed from the site in order to carry out repair work on the pump and replace the power supply unit. Additional repairs were also carried out on the sample line, which was slightly leaking. The unit was reinstalled in March.

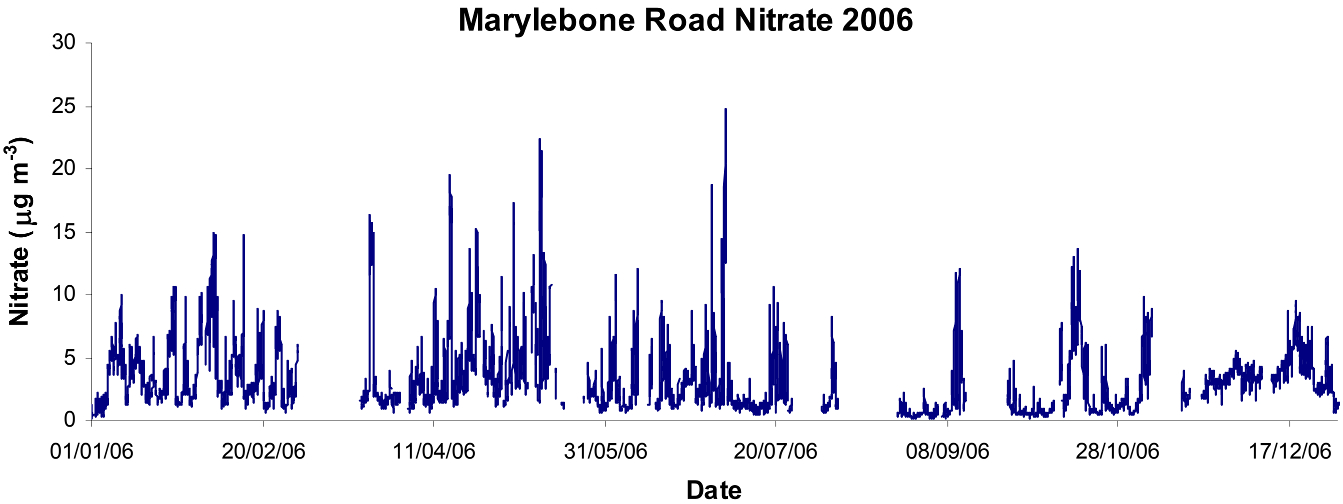


Figure 5c. Nitrate concentrations at Marylebone Road during 2006

Some data was lost during March at Marylebone Road due to a software fault on the NOx analyser. It was replaced with a spare by Air Monitors following a callout request.

Elevated levels of nitrate were recorded at all sites during the period 17/12/06 to 24/12/06 due to the foggy, still weather conditions in the UK at that time. Similar peaks are also seen in heavy metals, black smoke and PM_{10} data.

Partisol 2025

Monthly data capture rates for the Partisol 2025 instruments during 2006 are displayed in the table below:

Site	Belfast	Harwell	North Kensington	Marylebone Road
January	100%	100%	100%	100%
February	100%	100%	100%	82%
March	97%	100%	100%	97%
April	100%	100%	77%	97%
May	100%*	100%*	100%*	90%*
June	90%	97%	97%	93%
July	100%	100%	97%	77%
August	94%	100%	100%	77%
September	100%	80%	100%*	93%
October	81%*	23%*	100%	100%
November	100%	100%	97%	100%*
December	100%	52%	97%	100%
Average	**97%**	**87%**	**97%**	**92%**

* Month in which service was performed

Table 6. Monthly data capture for Partisol 2025 instruments during 2006

The Equipment Support Unit carries out services and instrument calibrations twice a year. Up to one day has been allowed for each of these service visits and that is reflected in the data capture calculation. An 'available' day has been removed from Harwell during February to account for the site move.

Low data capture was recorded in October at Harwell due to the destruction of the Partisol power cable by rodents. The data collection software at King's College London flagged the lack of data from the instrument, and a callout was issued for the repair.

Particulates collected by the Partisol instruments are analysed for sulphate, as required by Defra. Analyses for nitrate and chloride are also carried out. This data is displayed in the following graphs:

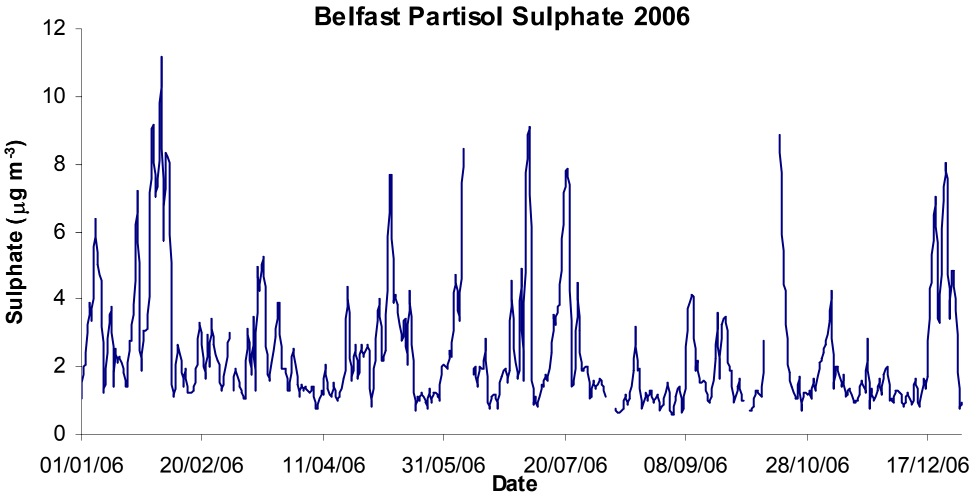


Figure 6a. **Sulphate concentrations at Belfast during 2006**

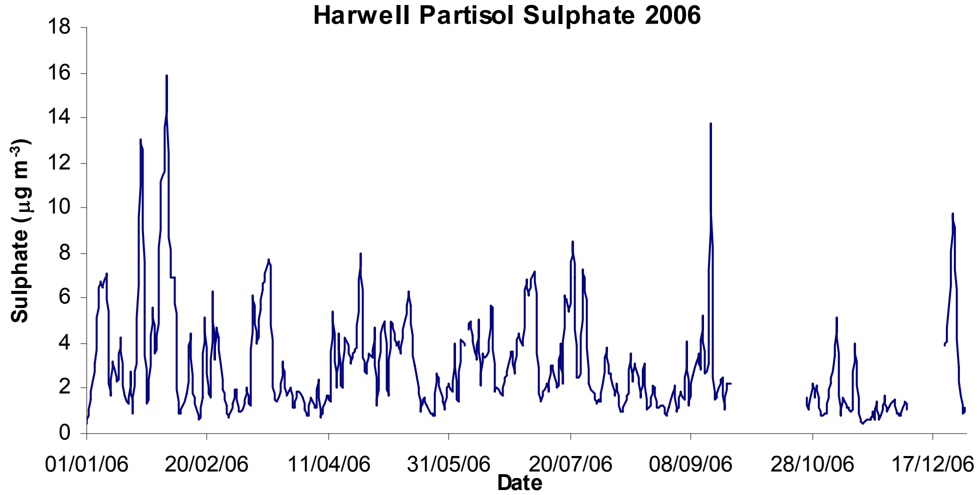


Figure 6b. **Sulphate concentrations at Harwell during 2006**

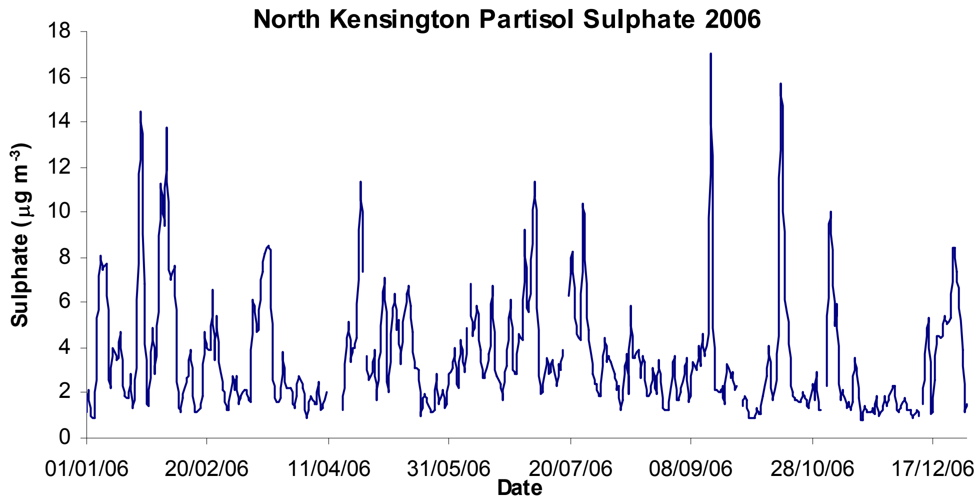


Figure 6c. **Sulphate concentrations at North Kensington during 2006**

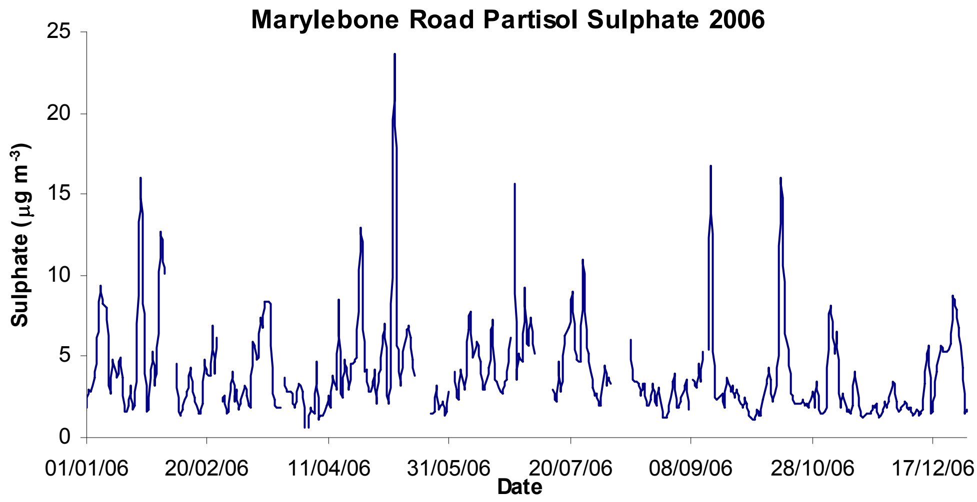


Figure 6d. **Sulphate concentrations at Marylebone Road during 2006**

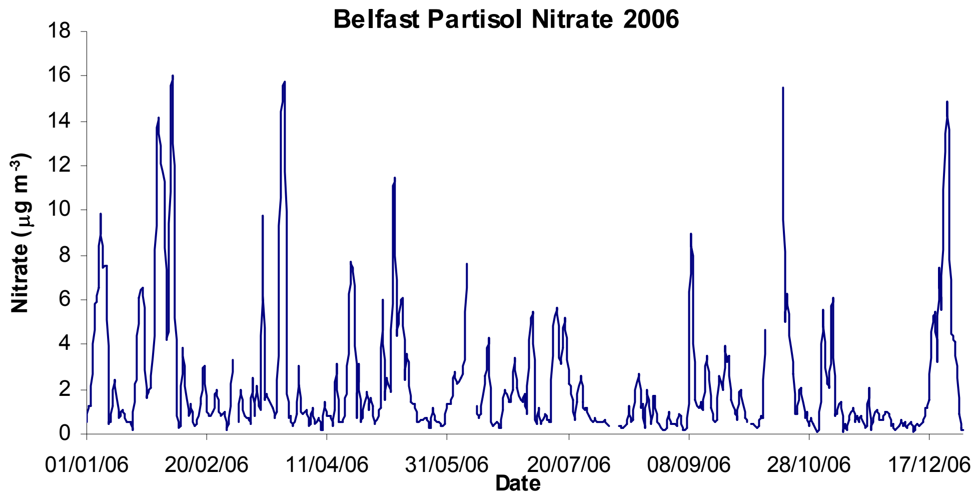


Figure 6e. **Nitrate concentrations at Belfast during 2006**

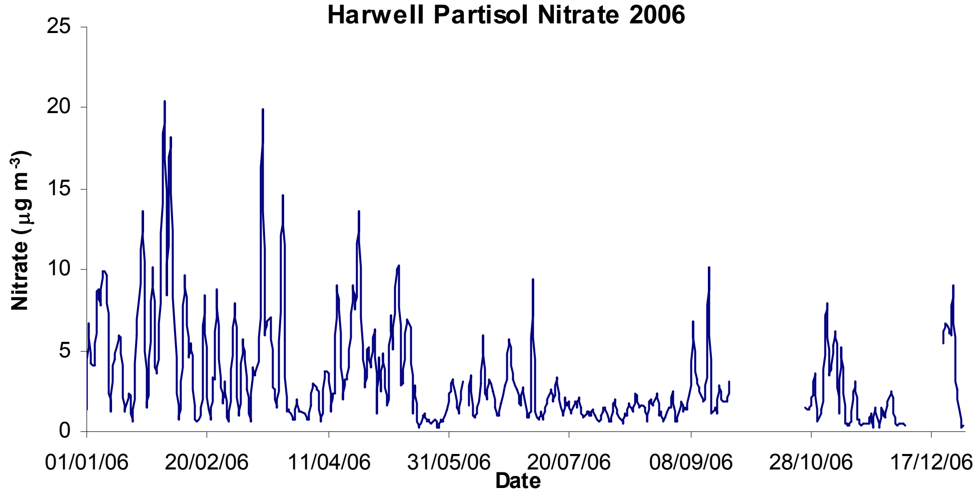


Figure 6f. **Nitrate concentrations at Harwell during 2006**

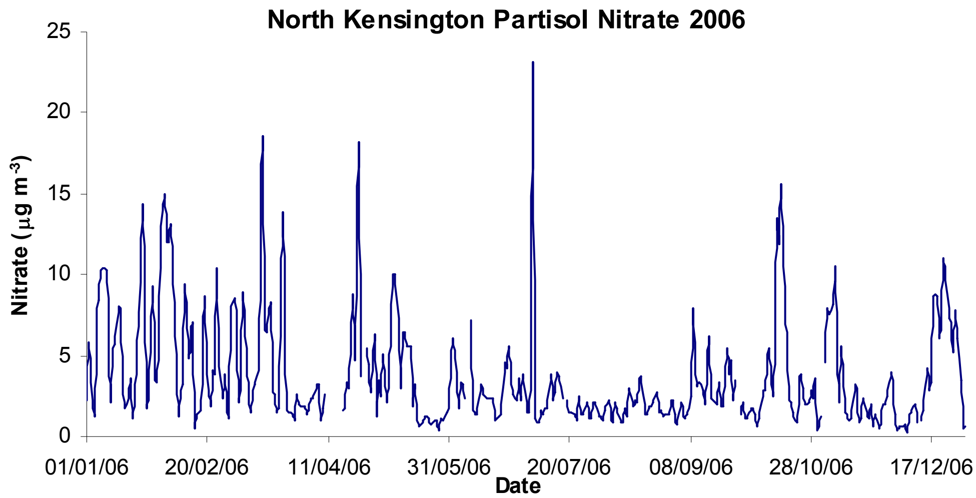


Figure 6g. Nitrate concentrations at North Kensington during 2006

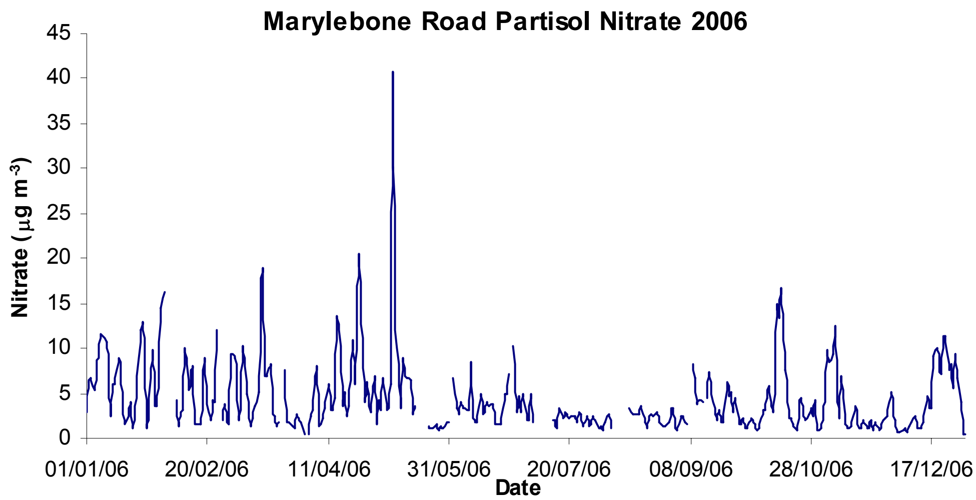


Figure 6h. Nitrate concentrations at Marylebone Road during 2006

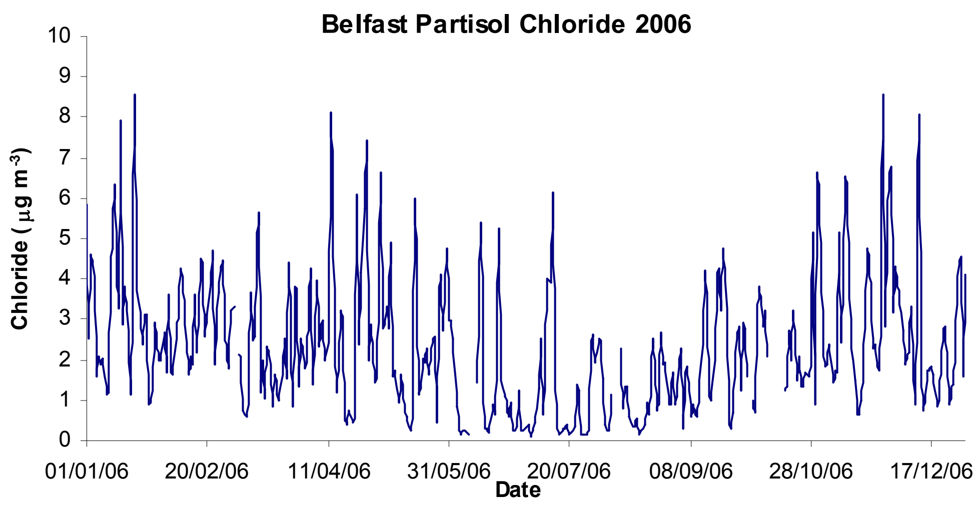


Figure 6i. Chloride concentrations at Belfast during 2006

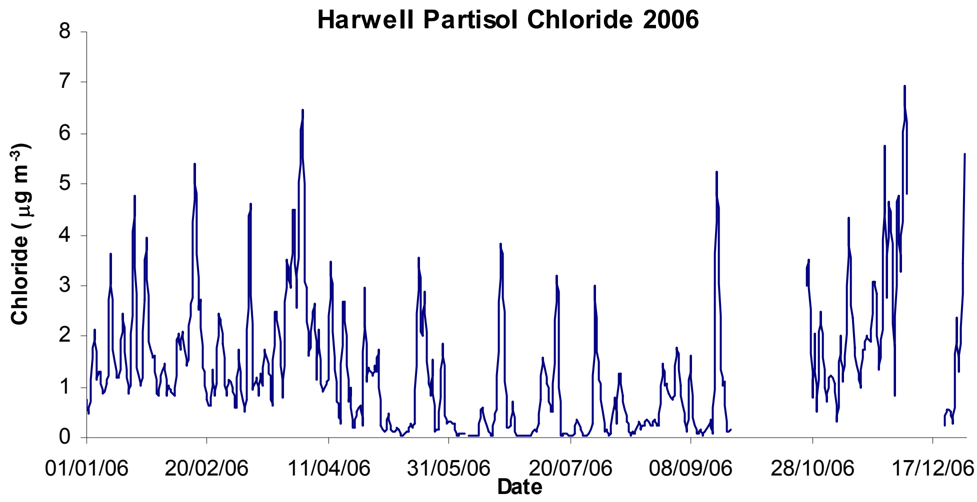


Figure 6j. **Chloride concentrations at Harwell during 2006**

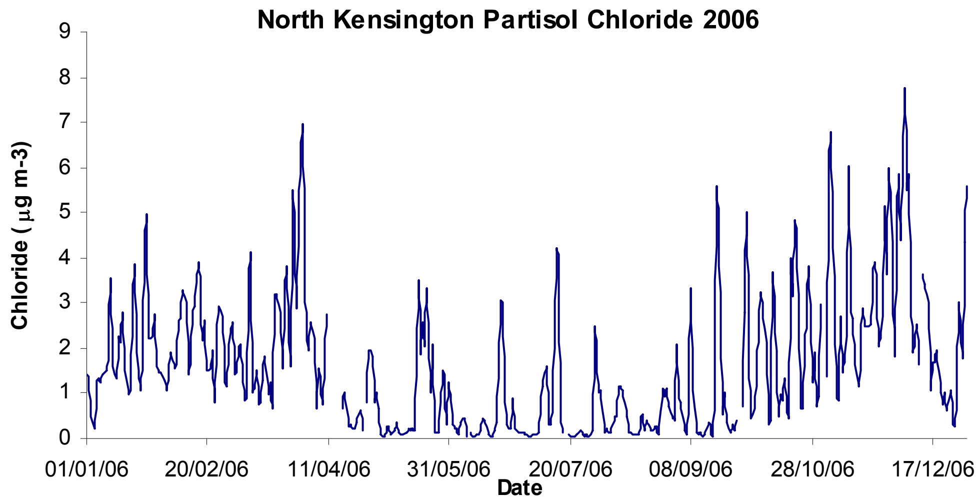


Figure 6k. **Chloride concentrations at North Kensington during 2006**

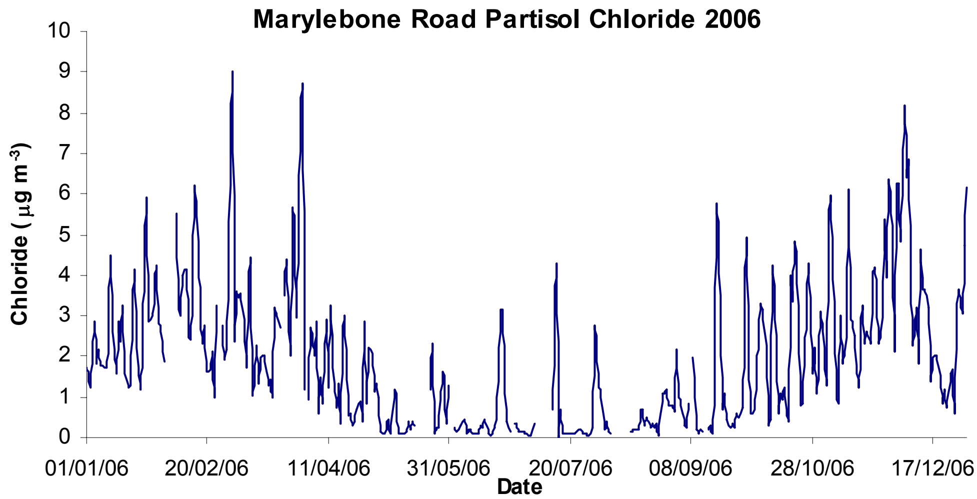


Figure 6l. **Chloride concentrations at Marylebone Road during 2006**

Comparison of Automatic Nitrate ($PM_{2.5}$) and Partisol 2025 Nitrate (PM_{10})

In the scatter plots, Figure 6m to Figure 6p, days where the data capture was less than 20 hours have been excluded.

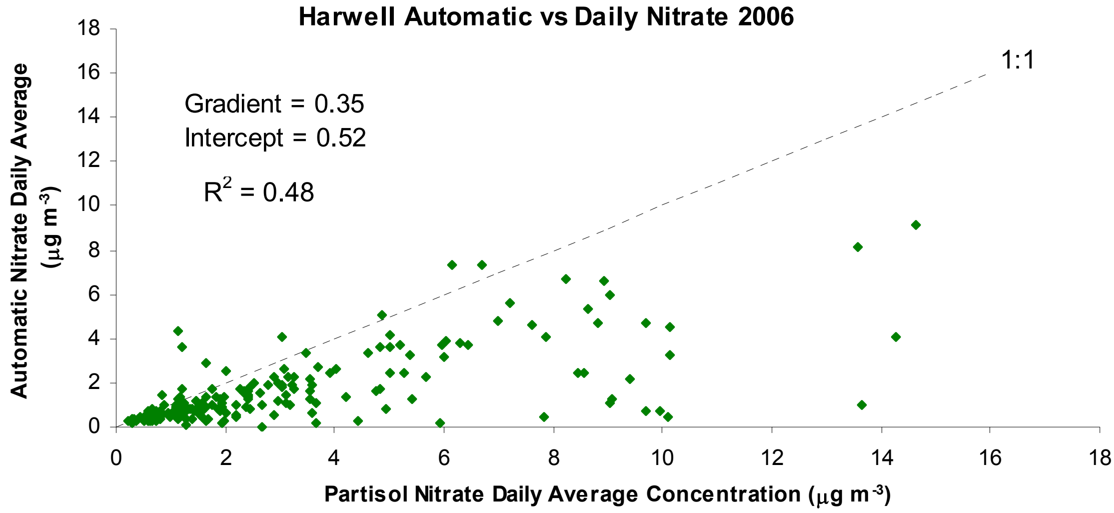


Figure 6m. Scatter plot of Nitrate concentrations at Harwell during 2006

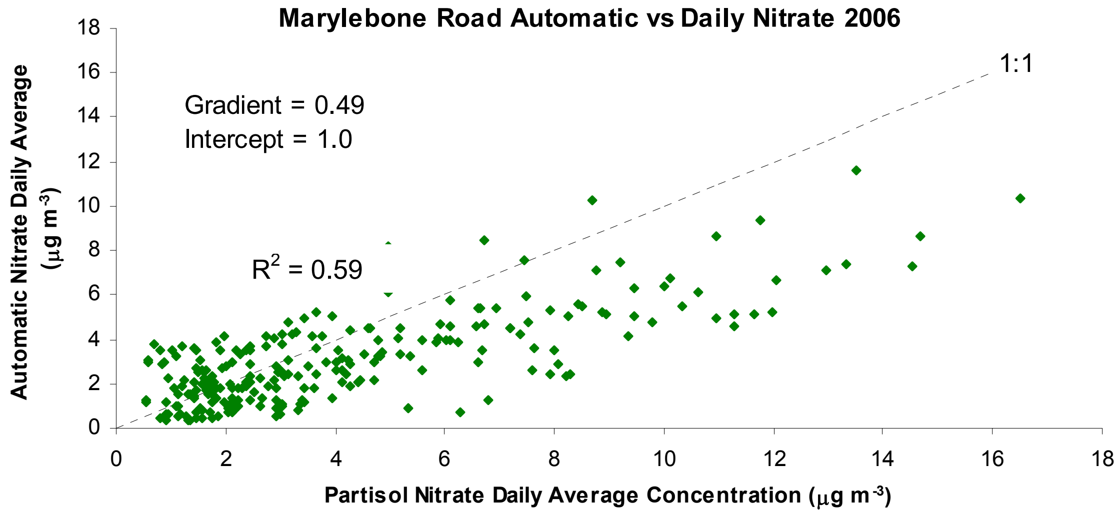


Figure 6n. Scatter plot of Nitrate concentrations at Marylebone Road in 2006

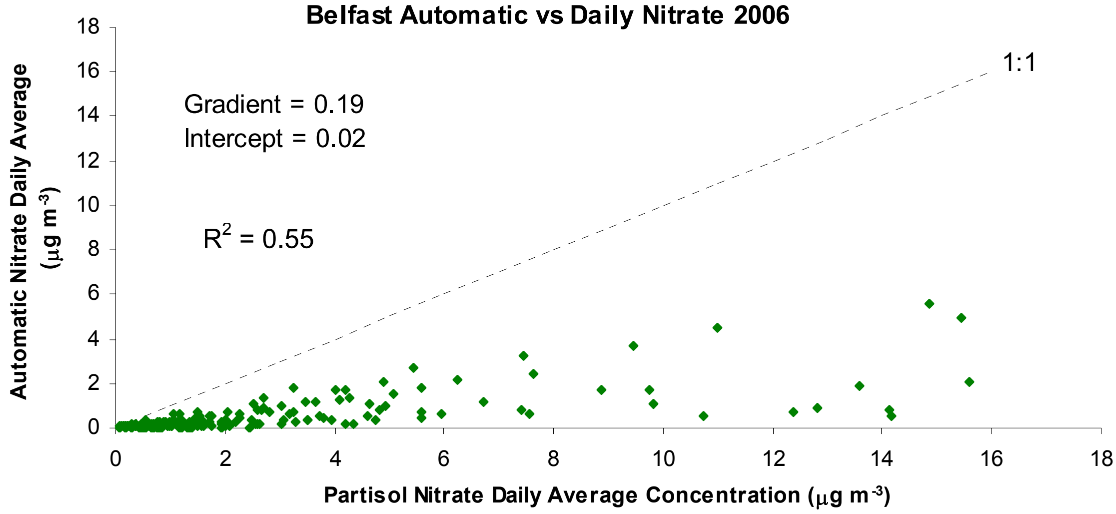


Figure 6p. Scatter plot of Nitrate concentrations at Belfast during 2006

These correlations are consistent with those found in previous years. The differences in the two measurement methods gives rise to the discrepancy in the results, and these are described in more detail in the recent NPL uncertainty report [3].

Scanning Mobility Particle Sizer (SMPS)

The SMPS (TSI model 3071) instruments ceased operation in March 2006, with the agreement of Defra. They were no longer supported by the manufacturer and had not been serviced or calibrated for some time. The instruments continued to measure particulates until they stopped working. However, this data cannot be properly ratified due to the lack of calibration data.

Monthly data capture rates for the SMPS instruments during 2006 are displayed in the table below:

Site	Harwell	London Bloomsbury	Marylebone Road
January	100%	0%	61%
February	85%	0%	0%
March	2%	3%	0%

Table 7. Monthly data capture for SMPS instruments during 2006.

Total particulate counts (between 12nm and 450nm diameter) at Harwell and Marylebone Road (when available) have been plotted in the figures on the following page. Full data sets, including size distributions, have been made available for public dissemination. In both cases, this data is indicative only, not ratified.

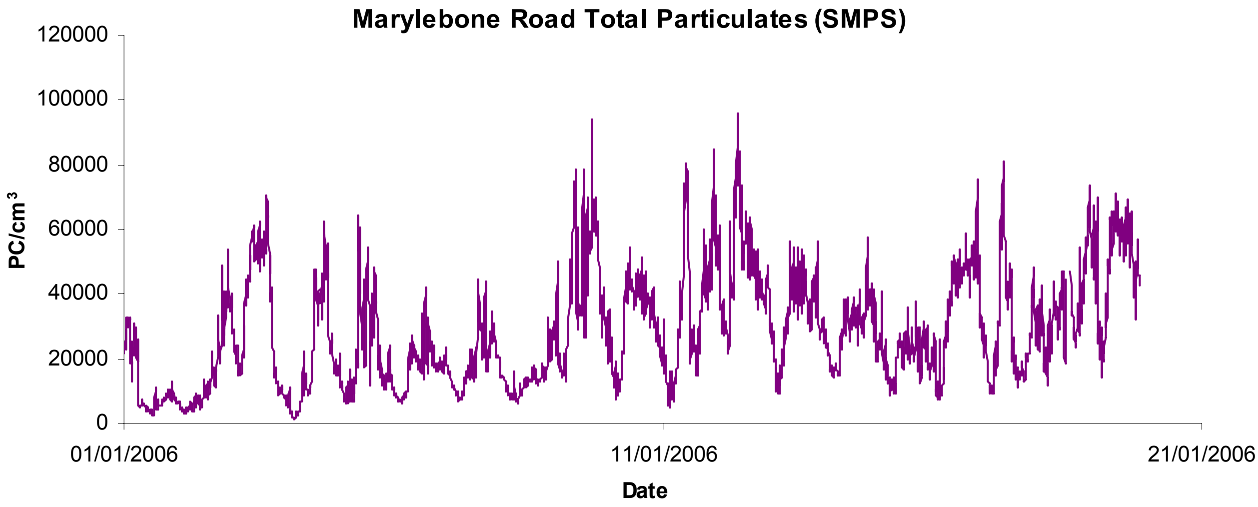


Figure 7a. **SMPS total particle count at Marylebone Road during 2006**

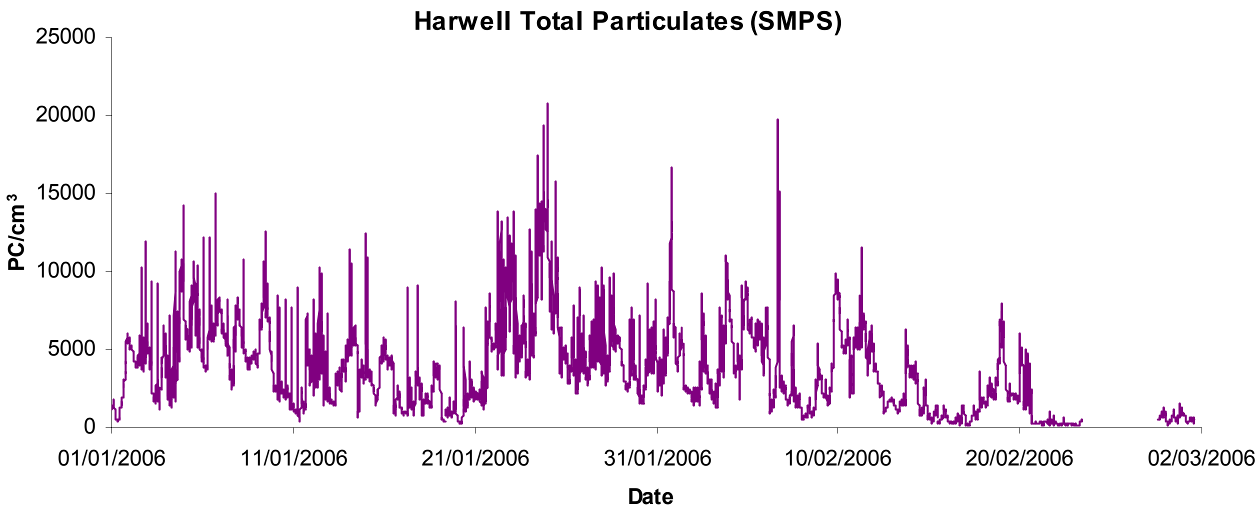


Figure 7b. **SMPS total particle count at Harwell during 2006.**

The graphs in Figure 7c indicate the size distribution of the particles measured at Harwell and Marylebone. Bloomsbury has been omitted due to the very low data capture. For the same reason, only certain months are shown for the other sites. The average size distributions for 2005 have also been included as a reference.

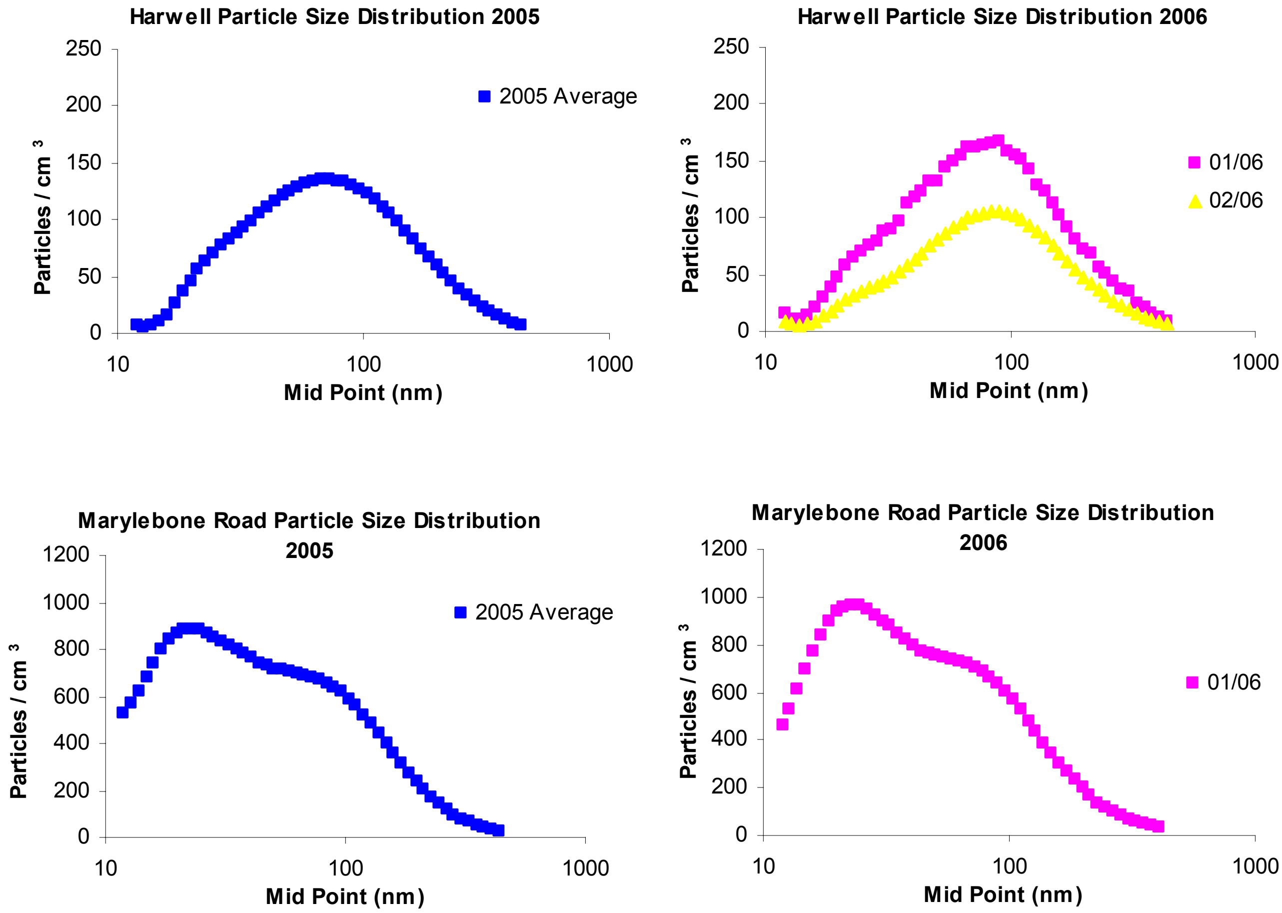


Figure 7c. Particle Size Distributions in 2006

The number and size distributions of the particulate matter at both Marylebone Road and Harwell are consistent with those in 2005. At Marylebone Road, a roadside site, the most commonly detected particles are smaller in size compared to the rural Harwell. The peak in the 2006 Marylebone Road graph is at 24.5nm, which is expected due to the small size (~30nm diameter) of diesel particles. It can also be noted that the number of particles per cubic centimetre is also much higher at the roadside site.

Condensation Particle Counter (CPC)

Monthly data capture rates for the CPC instruments during 2006 are displayed in the table below. Each instrument is removed from the site for a full service and calibration annually. This scheduled maintenance is expected to take three weeks, to include draining and drying, transit time, full service at TSI Instruments, and re-installation. In the month(s) where the CPC was serviced, the data capture quoted in the table takes into account the scheduled downtime, and is denoted with an asterisk.

Site	Belfast	Birmingham	Glasgow	North Kensington	Marylebone Road	Manchester	Port Talbot
January	16%	24%	95%	97%	97%	100%	100%
February	94%*	92%	99%	100%	79%	100%	100%
March	97%	100%	93%	84%	0%	100%	97%
April	100%	100%	100%	83%*	90%	100%	100%
May	100%	100%	100%	91%	97%	100%	100%
June	97%	97%	97%	97%	91%	97%	97%
July	100%	53%	94%	93%	84%	100%	100%
August	100%	68%*	99%	85%	100%	84%	98%
September	92%	72%	100%	84%	60%	90%	70%*
October	93%	99%	97%	97%	92%*	76%*	63%
November	100%	100%	97%*	100%	100%	92%*	100%
December	100%	99%	82%	100%	99%	100%	83%
Average	**91%**	**84%**	**96%**	**93%**	**83%**	**95%**	**93%**

Table 8. Monthly data capture for CPC instruments during 2006.

Graphs of the particle numbers (between 7nm and several microns in diameter) measured at each site are shown below:

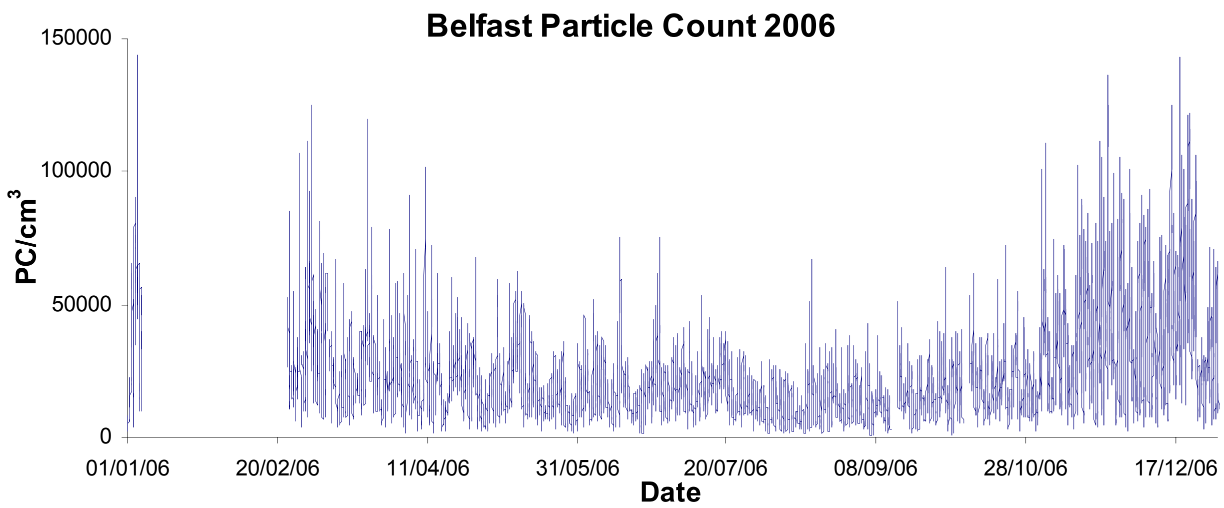


Figure 8a. CPC particle count at Belfast during 2006.

The Belfast CPC was drained in preparation for its annual service and calibration on 03/01/06. The transportation and service procedures took longer than the reasonable three-week period usually allocated for this task. As a result the instrument was not reinstalled until 22/02/06.

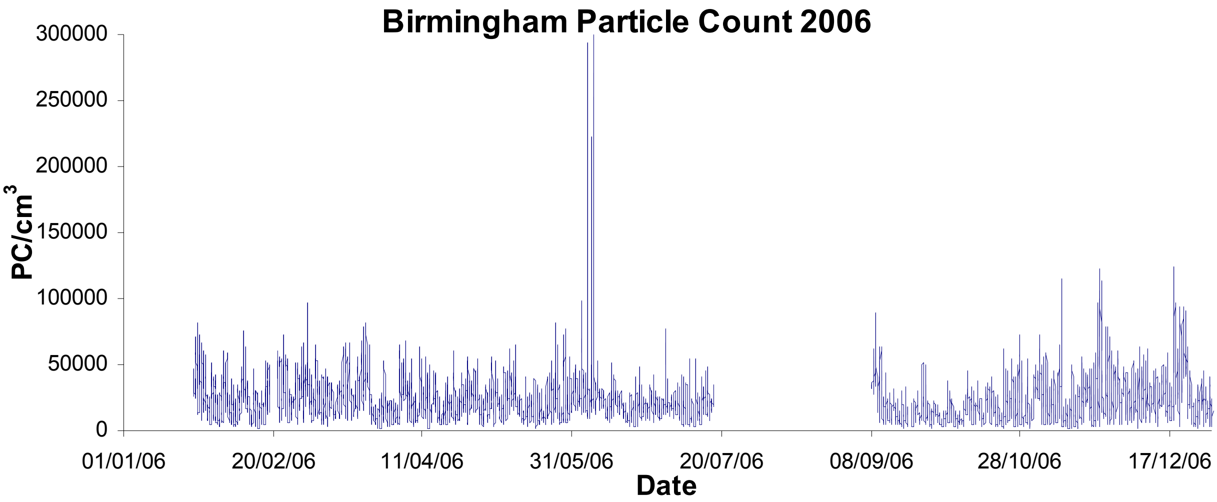
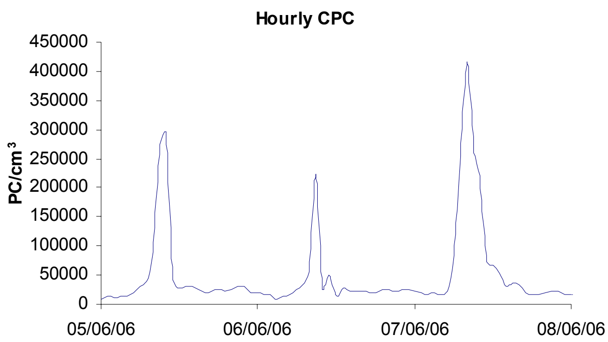


Figure 8b. CPC particle count at Birmingham during 2006.

In December 2005, the automatic data logging and validation system at King's College London identified a problem with the CPC flow at Birmingham. The instrument was returned to the manufacturer for repair and was returned to the site on 24/01/06.

There was an episode of high particle counts on three mornings during June, as indicated in Figure 8c. These occurred during the hours of 8am and 12pm each day and correlated with the local PM_{10} measurements.



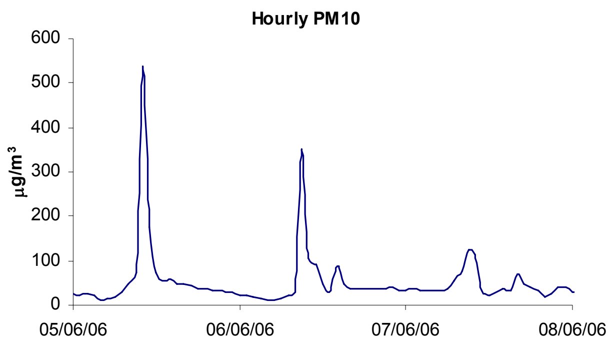


Figure 8c. Hourly Particle Counts and PM_{10} mass during 5th -8th June 2006

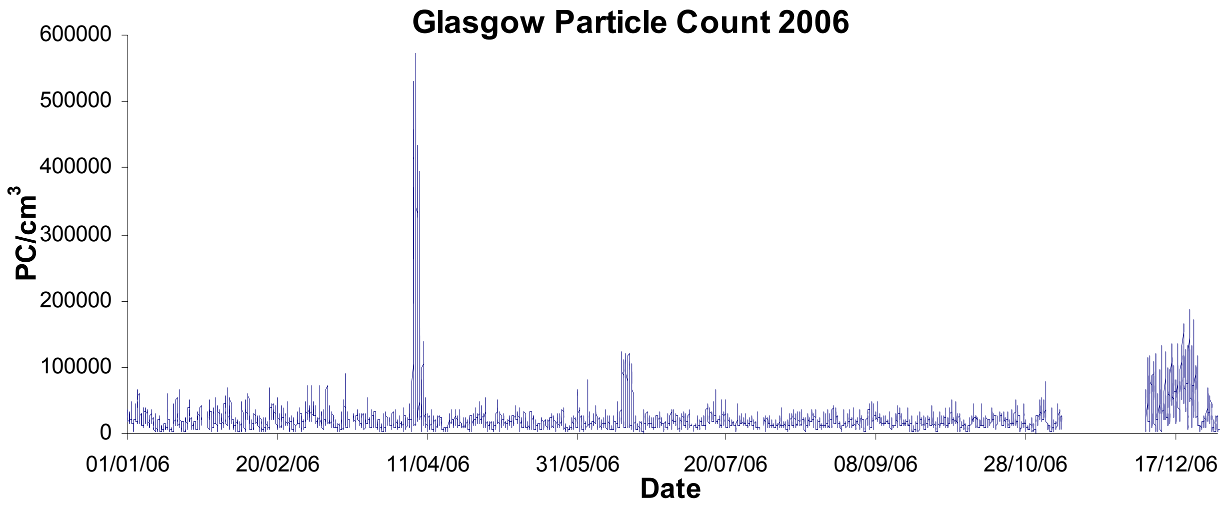


Figure 8d. CPC particle count at Glasgow during 2006.

The CPC at St Enoch's Square in Glasgow tends to experience spikes in particulate matter at various times throughout the year due to food markets, which are occasionally held in the Square. This was the case in April (a farmers' market, where a diesel generator was parked next to the CPC), June, and December (a German Christmas market). Slightly elevated levels are seen in the hourly PM_{10} data, but not to the same extent that is measured by the CPC, suggesting a large number of particles with low mass, i.e fine particles.

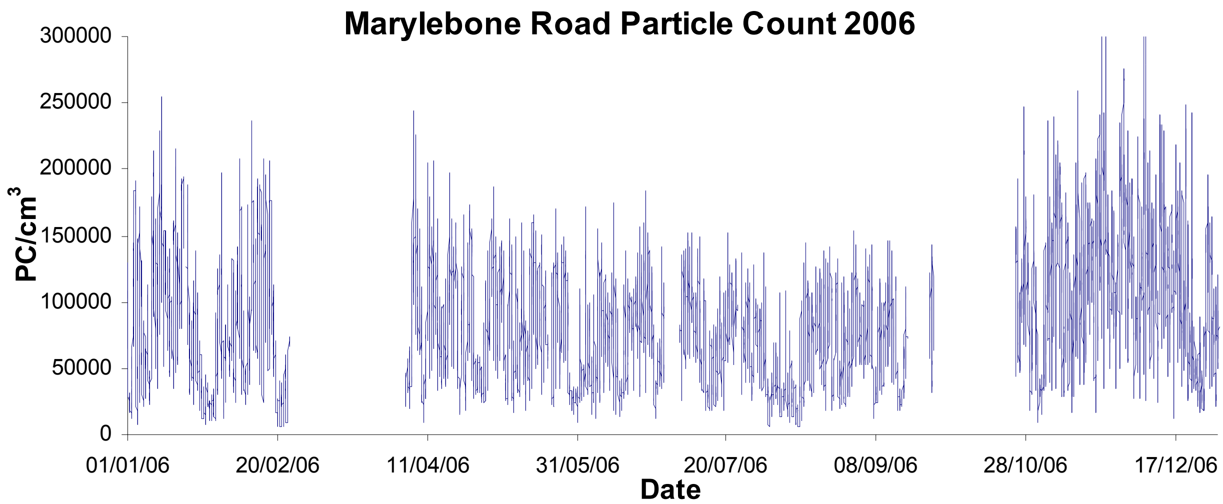


Figure 8e. CPC particle count at Marylebone Road during 2006.

During February the Marylebone Road CPC experienced pump problems. It was returned to the manufacturer, TSI, for repair. The instrument was calibrated in October.

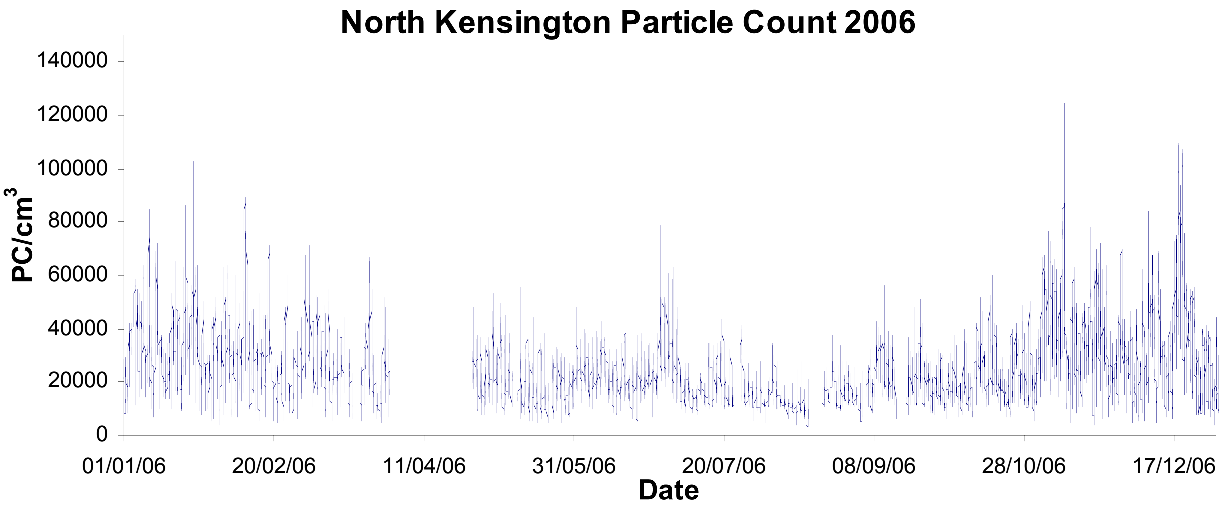


Figure 8f. **CPC particle count at North Kensington during 2006.**

The North Kensington instrument was serviced and calibrated during April.

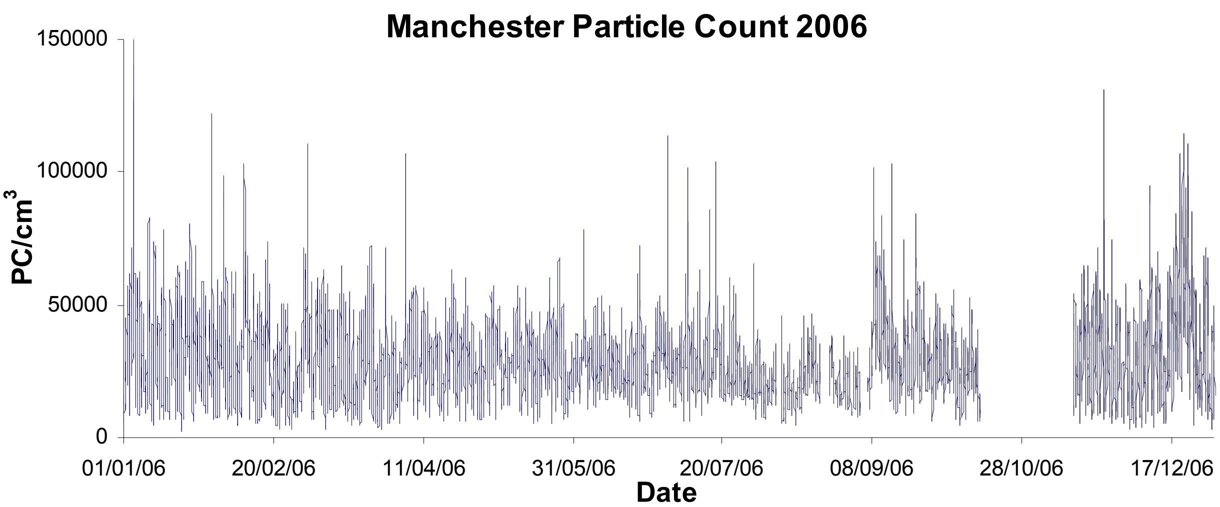


Figure 8g. **CPC particle count at Manchester during 2006.**

The Manchester CPC was at TSI for service and calibration for part of October and November.

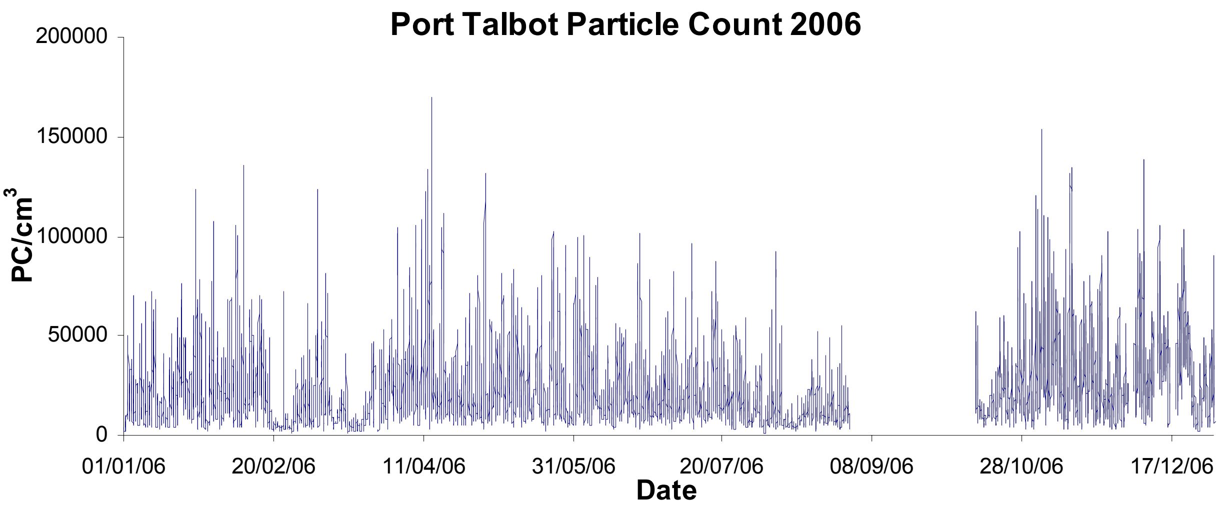


Figure 8h. CPC particle count at Port Talbot during 2006.

The Port Talbot CPC was serviced and calibrated in September 2006.

SMPS versus CPC data

The discrepancy between particle counts from TSI SMPS and CPC instruments has been well documented, and ratios of the measurements from the two instruments have been presented in previous reports to Defra. In January 2006 SMPS and CPC instruments were collocated at Marylebone Road. Unfortunately this is the only month during which we have data for the SMPS.

The following figure shows the relationship between CPC particle number count and SMPS particle number count.

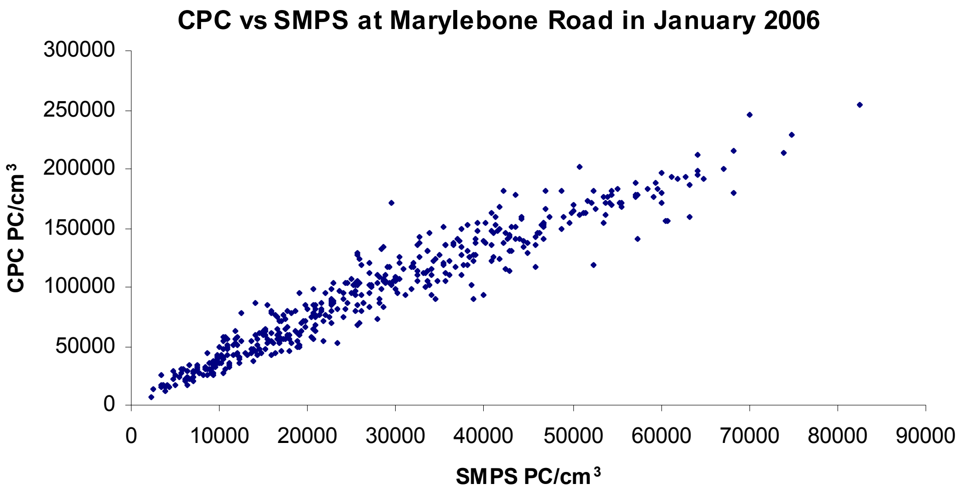


Figure 8i. Scatter plot of CPC and SMPS particle counts at Marylebone Road in January 2006

This scatter plot shows a very similar relationship to that seen in the latter months of 2005, as shown in the table of ratios of the CPC to SMPS total counts:

July 2005	2.7
August 2005	2.4
September 2005	2.3
October 2005	2.5
November 2005	2.6
December 2005	2.6
January 2006	3.0

Table 9. Monthly ratio of CPC to SMPS particle counts

The difference in the particle counts from the collocated CPC and SMPS is partly due to some particle losses inside the SMPS classifier. The instrument software does make a correction for this but it is unlikely to be 100% accurate. Additionally, and more importantly, the two instruments measure different particles - the CPC can detect particles from about 7nm up to several microns in diameter. The SMPS, however, is only capable of counting particles in the range 12nm to 450nm.

Meteorological Mast

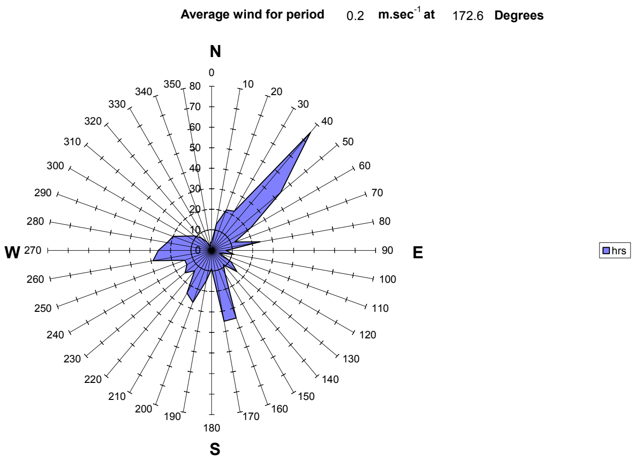
Monthly data capture rates for the Meteorological Masts during 2006 are displayed in the table below:

Site	Harwell	Rochester
January	99%	99%
February	100%	99%
March	98%*	100%
April	99%	99%
May	98%	99%
June	98%	100%
July	99%	100%
August	99%	99%
September	99%	97%
October	99%	100%
November	97%	96%
December	100%	85%
Average	99%	98%

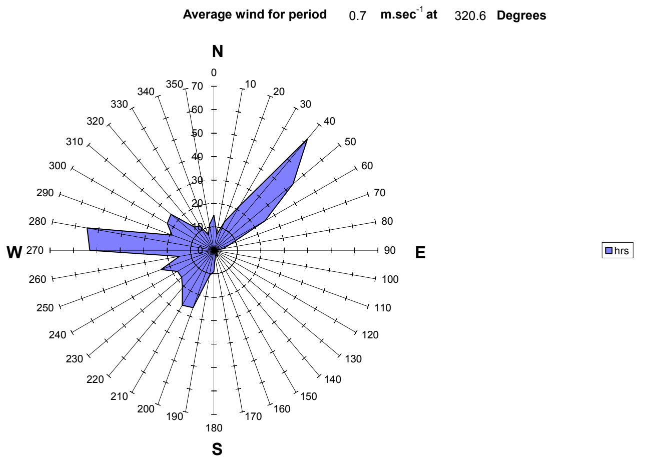
Table 10. Monthly data capture for Meteorological instruments during 2006.

* 24 days in March were used for mast relocation and have been removed from the available time.

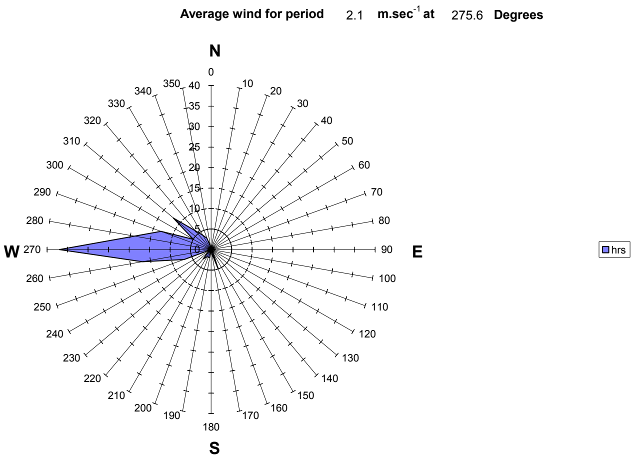
Wind roses for Harwell and Rochester are presented in the following figures.



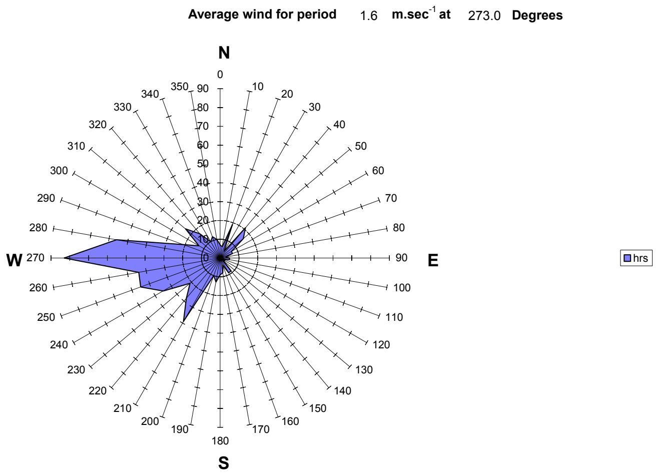
Harwell January 2006



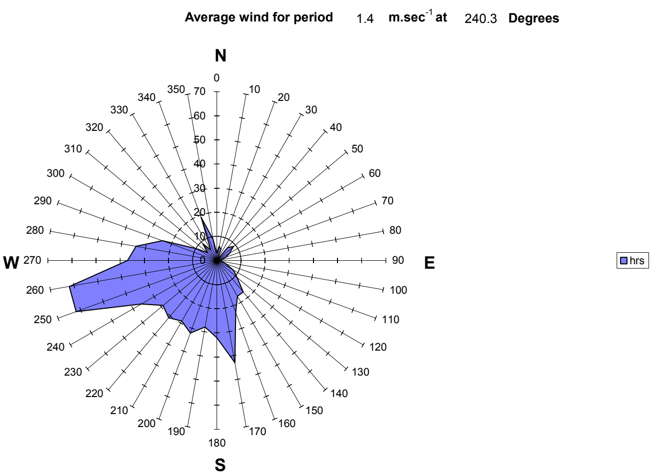
Harwell February 2006



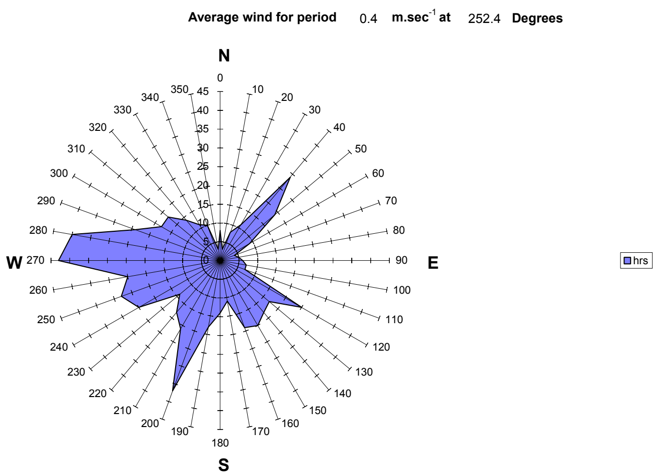
Harwell March 2006



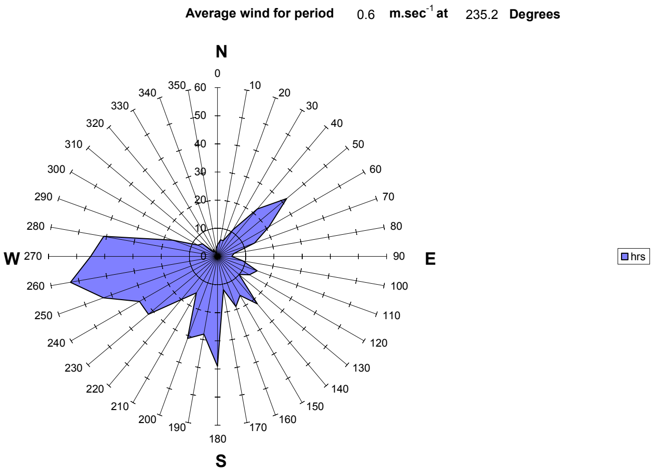
Harwell April 2006



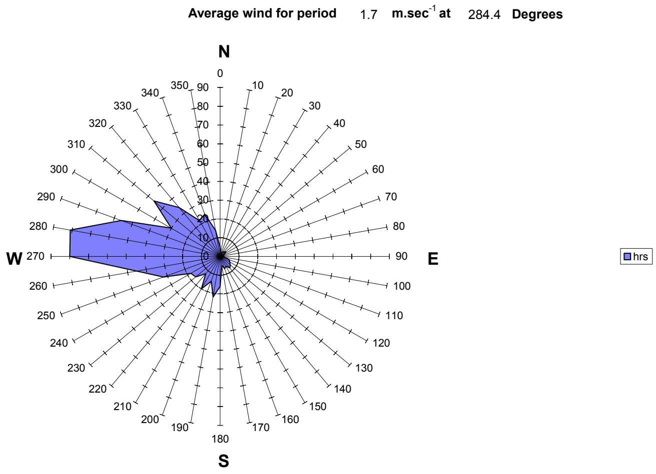
Harwell May 2006



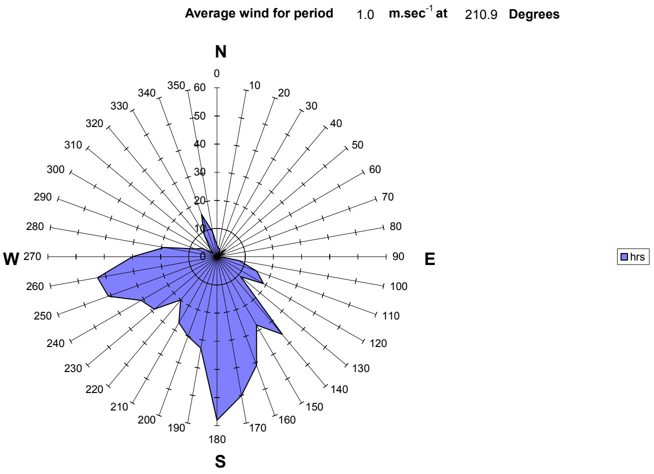
Harwell June 2006



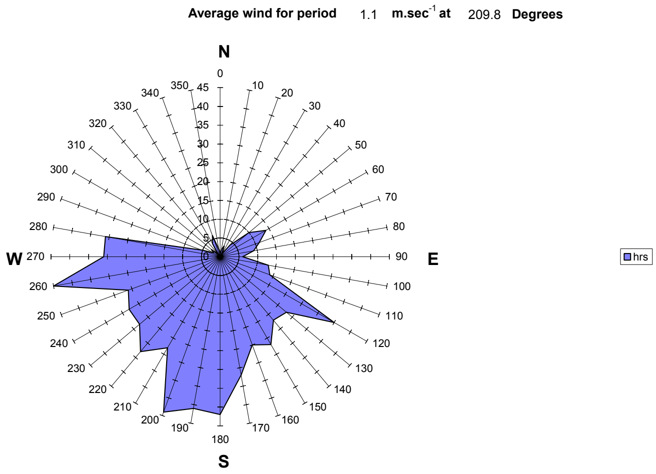
Harwell July 2006



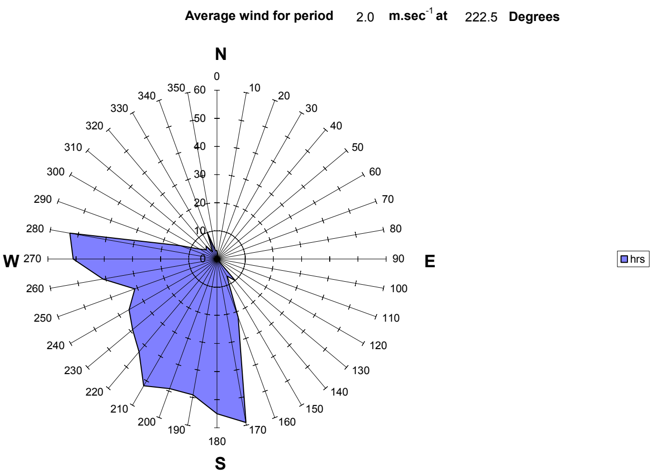
Harwell August 2006



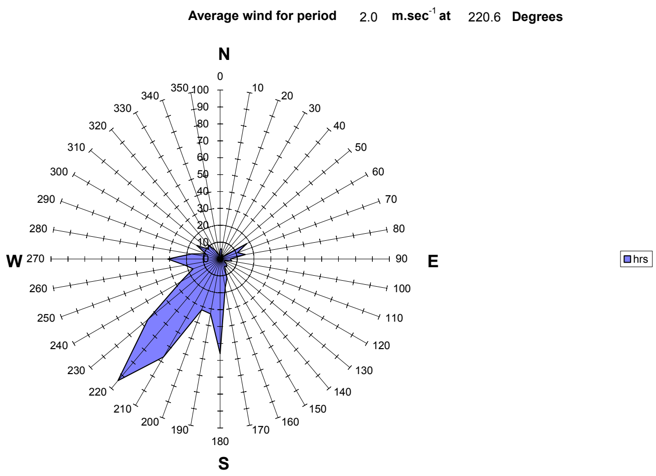
Harwell September 2006



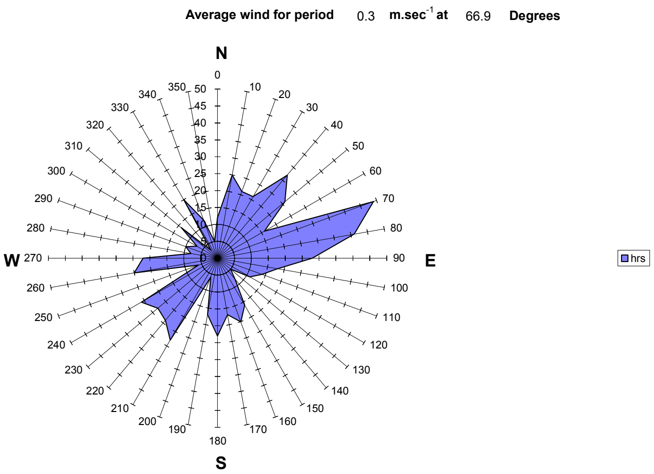
Harwell October 2006



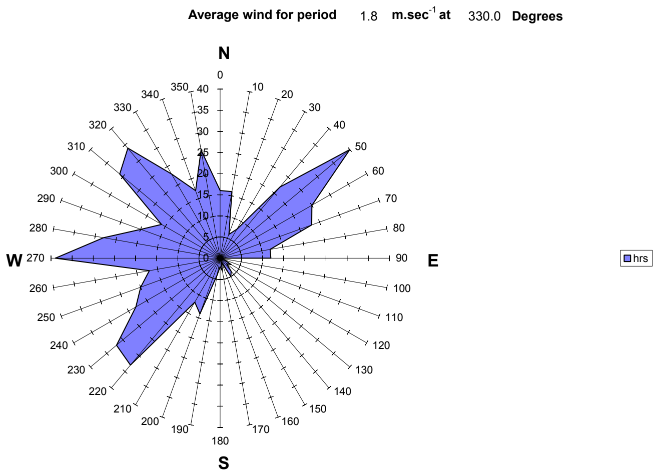
Harwell November 2006



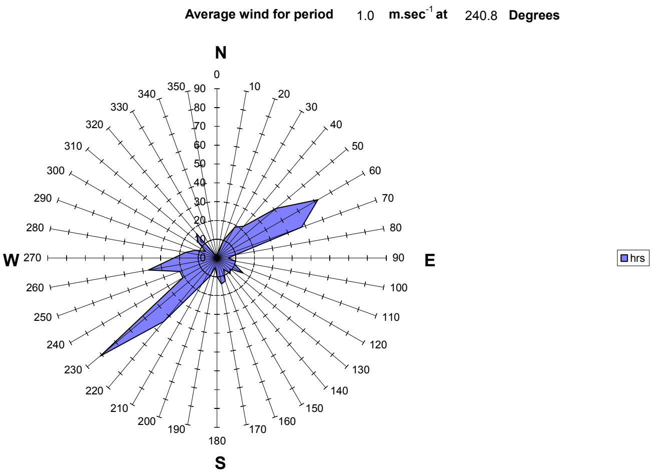
Harwell December 2006



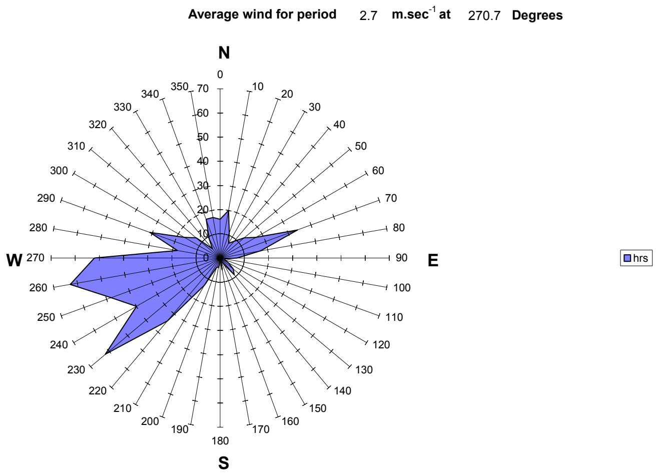
Rochester January 2006



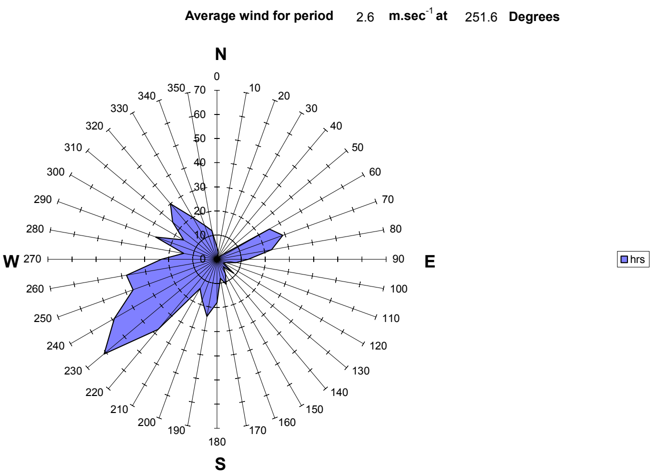
Rochester February 2006



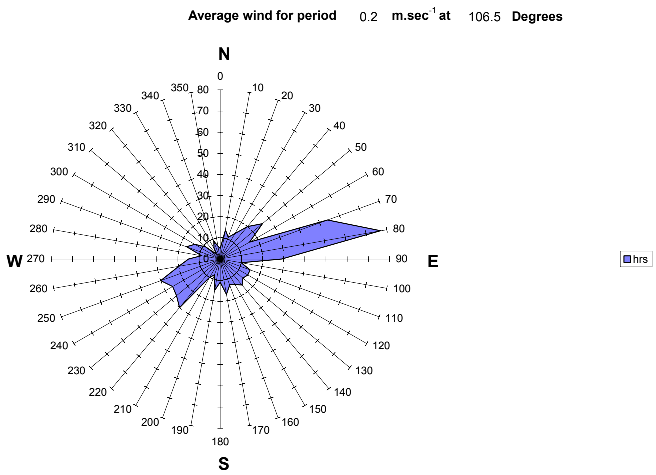
Rochester March 2006



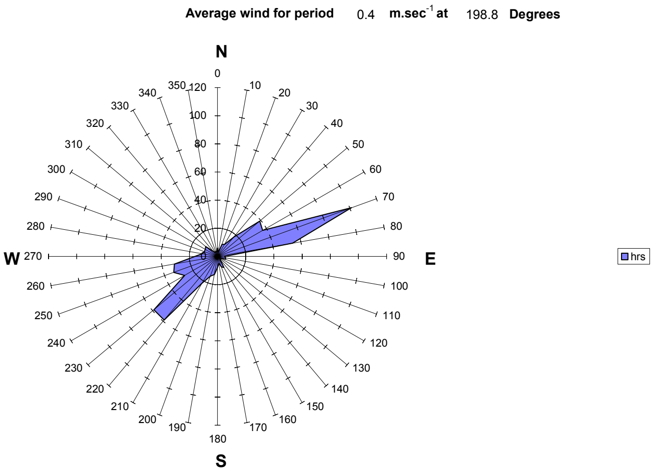
Rochester April 2006



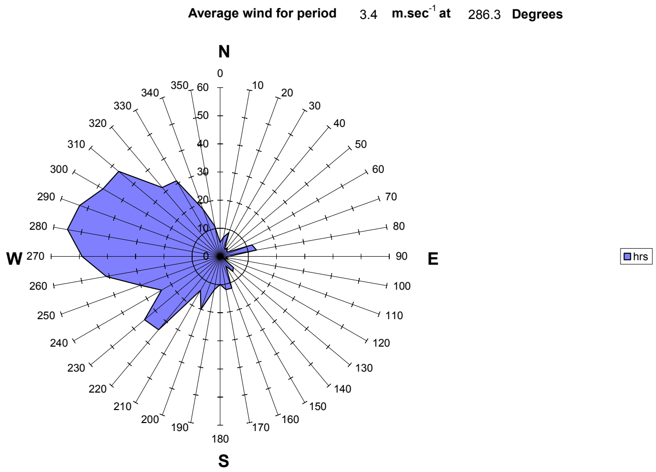
Rochester May 2006



Rochester June 2006



Rochester July 2006



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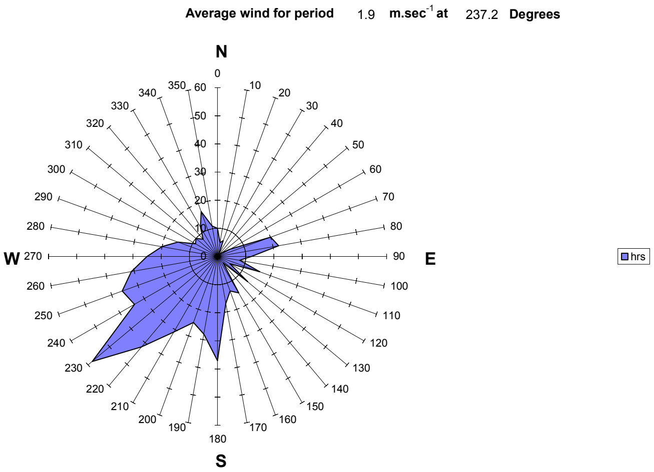

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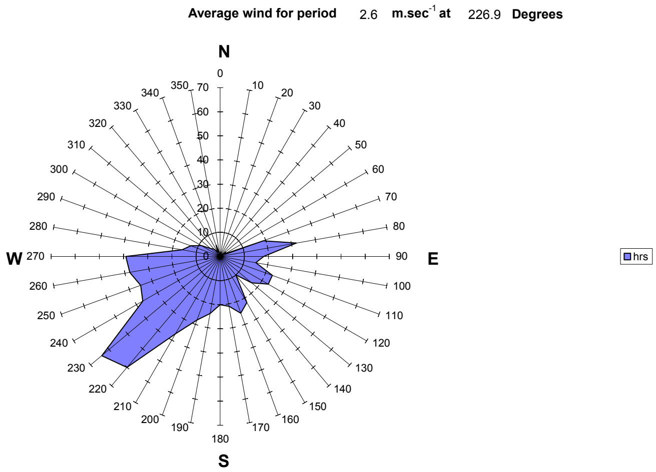

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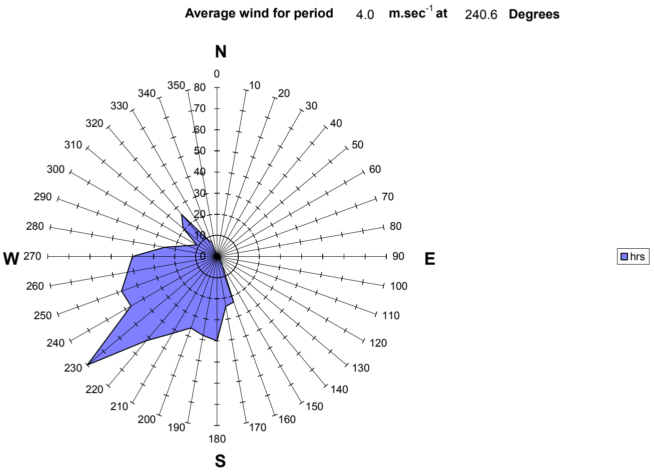

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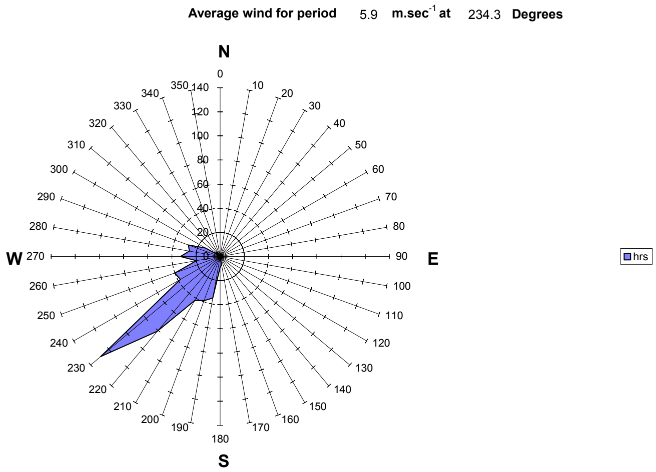


Rochester December 2006

Summary of Yearly Means

Instrument	2003 Mean	2004 Mean	2005 Mean	2006 Mean	Units
Belfast Carbon (organic)	2.96	2.99	0.87	2.84	$\mu g.m^{-3}$
Belfast Carbon (elemental)	0.71	0.72	1.16	0.76	$\mu g.m^{-3}$
Belfast Carbon (Total)	3.67	3.71	2.03	3.60	$\mu g.m^{-3}$
Harwell Carbon (organic)	2.22	1.18	0.44	0.65	$\mu g.m^{-3}$
Harwell Carbon (elemental)	0.77	0.54	1.03	0.42	$\mu g.m^{-3}$
Harwell Carbon (Total)	2.99	1.72	1.47	1.07	$\mu g.m^{-3}$
Marylebone Road Carbon (organic)	4.54	4.28	4.17	6.73	$\mu g.m^{-3}$
Marylebone Road Carbon (elemental)	3.35	2.42	1.64	2.96	$\mu g.m^{-3}$
Marylebone Road Carbon (Total)	7.89	6.7	5.81	9.68	$\mu g.m^{-3}$
North Kensington Carbon (organic)	3.07	2.37	3.78	6.96	$\mu g.m^{-3}$
North Kensington Carbon (elemental)	1.15	0.64	0.84	2.98	$\mu g.m^{-3}$
North Kensington Carbon (Total)	4.22	3.01	4.62	9.92	$\mu g.m^{-3}$
Belfast Nitrate ($PM_{2.5}$)	0.70	0.52	0.44	0.48	$\mu g.m^{-3}$
Harwell Nitrate ($PM_{2.5}$)	2.66	4.27	1.94	1.61	$\mu g.m^{-3}$
Marylebone Road Nitrate ($PM_{2.5}$)	N/A	N/A	3.33	3.18	$\mu g.m^{-3}$
Belfast Daily Nitrate (PM_{10})	3.24	1.52	2.15	2.21	$\mu g.m^{-3}$
Harwell Daily Nitrate (PM_{10})	3.90	2.76	3.17	3.21	$\mu g.m^{-3}$
Marylebone Road Daily Nitrate (PM_{10})	5.06	3.93	3.97	4.39	$\mu g.m^{-3}$
North Kensington Daily Nitrate (PM_{10})	4.32	3.38	3.91	3.74	$\mu g.m^{-3}$
Belfast Daily Sulphate (PM_{10})	1.87	1.78	2.18	2.38	$\mu g\ m^{-3}$
Harwell Daily Sulphate (PM_{10})	2.44	2.29	2.40	3.01	$\mu g\ m^{-3}$
Marylebone Road Daily Sulphate (PM_{10})	3.18	3.16	3.21	4.00	$\mu g\ m^{-3}$
North Kensington Daily Sulphate (PM_{10})	2.61	2.95	3.02	3.51	$\mu g\ m^{-3}$
Belfast Daily Chloride (PM_{10})	1.82	1.96	1.98	2.30	$\mu g\ m^{-3}$
Harwell Daily Chloride (PM_{10})	0.91	1.04	1.19	1.32	$\mu g\ m^{-3}$
Marylebone Road Daily Chloride (PM_{10})	1.45	1.54	1.64	2.01	$\mu g\ m^{-3}$
North Kensington Daily Chloride (PM_{10})	1.11	1.24	1.33	1.57	$\mu g\ m^{-3}$
Belfast CPC	17632	16165	26190	22231	PC cm^{-3}
Birmingham CPC	17998	16752	20254	21684	PC cm^{-3}
Glasgow CPC	17075	14437	33718	21124	PC cm^{-3}
Manchester CPC	15622	13178	19965	28712	PC cm^{-3}
Marylebone Road CPC	N/A	70878	79606	83175	PC cm^{-3}
North Kensington CPC	21743	17664	22017	23946	PC cm^{-3}
Port Talbot CPC	15389	11583	13939	22870	PC cm^{-3}

Table 11. Yearly average concentrations and particle counts for Network instruments for 2003 – 2006

SMPS instruments are omitted from Table 11 because they are no longer supported by the manufacturer and, as such, cannot be serviced or calibrated. Automatic carbon results are included but are highlighted in red, as the data capture is often low and therefore not a representative average for the year, and because the results for 2005 and 2006 cannot be fully ratified.

The trends evident in this data are displayed graphically in Figure 9a to 9d. Carbon data is not included.

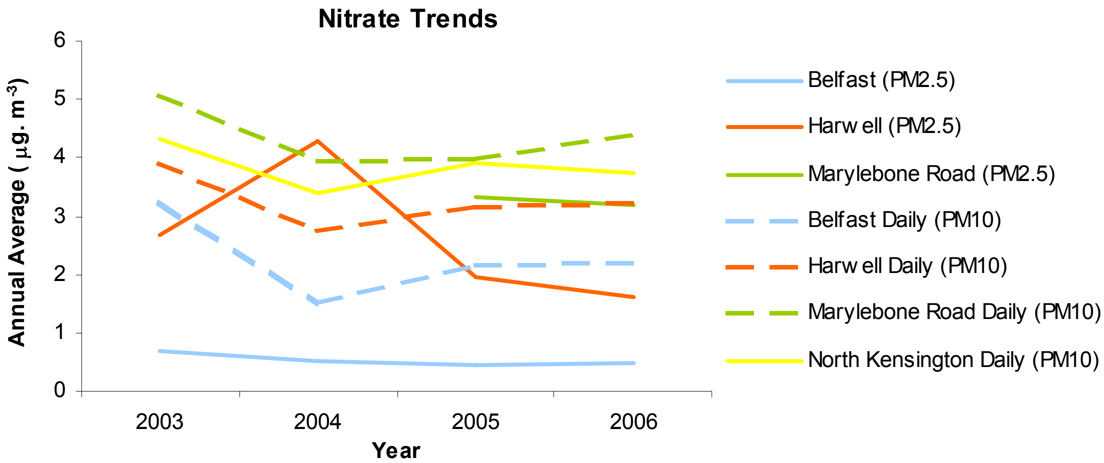


Figure 9a. Annual average nitrate concentrations 2003 - 2006

With the exception of an anomalous result at Harwell in 2004, nitrate (both $PM_{2.5}$ and PM_{10}) concentrations appear to have risen slightly since 2004, when recorded ambient levels were relatively low. Within the uncertainty of the measurements there is no significant change between 2005 and 2006.

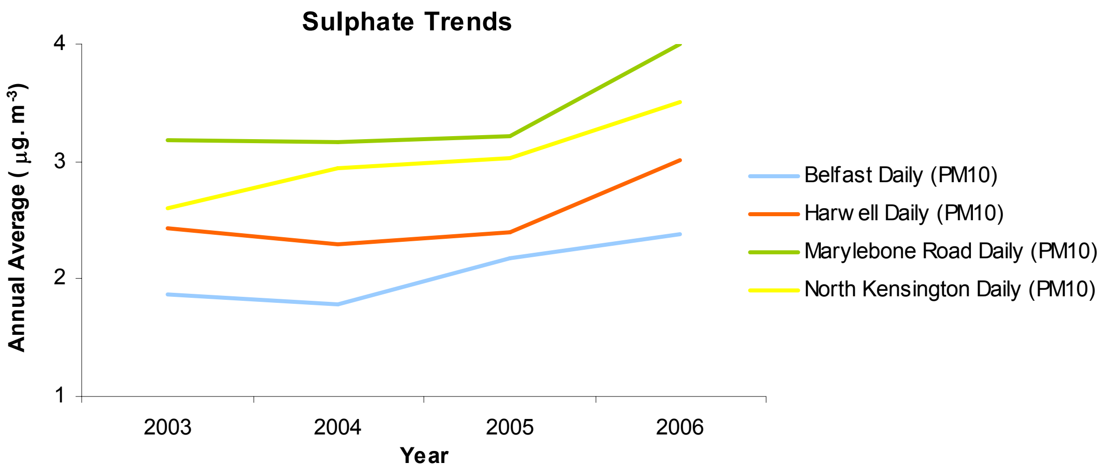


Figure 9b. Annual average sulphate concentrations 2003 - 2006

Average daily sulphate concentrations have increased at each site since 2003, particularly at the two London sites, and most significantly within the last year.

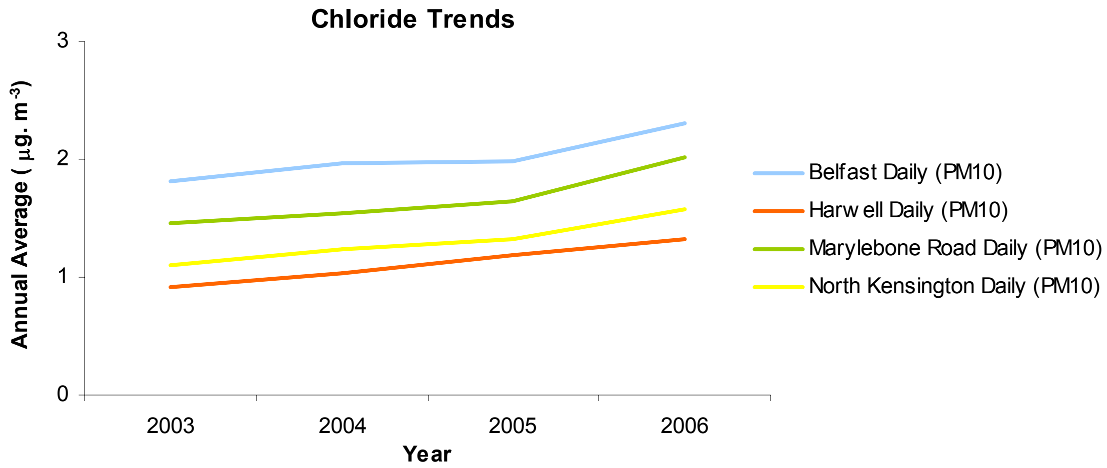


Figure 9c. Annual average chloride concentrations 2003 - 2006

Daily chloride concentrations are also seen to increase over the past few years. The increase is relatively steady and can therefore be assumed to be a real trend, rather than a random variation within the uncertainty of the measurement.

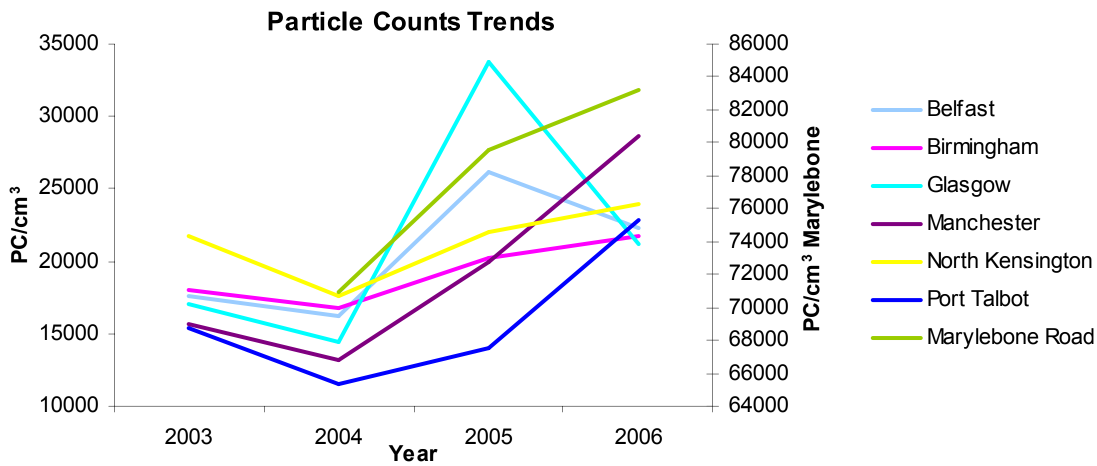


Figure 9d. Annual average particle counts 2003 - 2006

Since 2004, the average particle counts have increased at every site, in some locations the counts have risen sharply, particularly at Port Talbot and Manchester. The sharp peak at Glasgow in 2005 is influenced by the occasional markets held in St Enoch's Square, and is not representative of a usual day.

Diurnal Trends

For instruments that produce automatic 'continuous' data, it is possible to calculate the average result for each hour of the day. This data is shown graphically in Figures 10a to 10c for the nitrate analysers, and in Figure 10d for the CPCs.

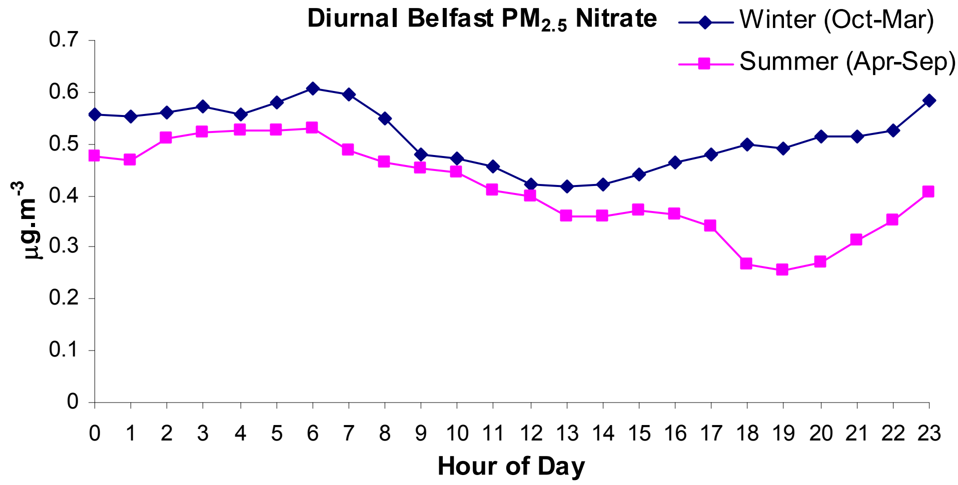


Figure 10a. Diurnal representation of Belfast Nitrate 2006

It can be seen that nitrate concentrations at Belfast are lower during the summer months, as would be expected due to the decomposition of ammonium nitrate at warm temperatures.

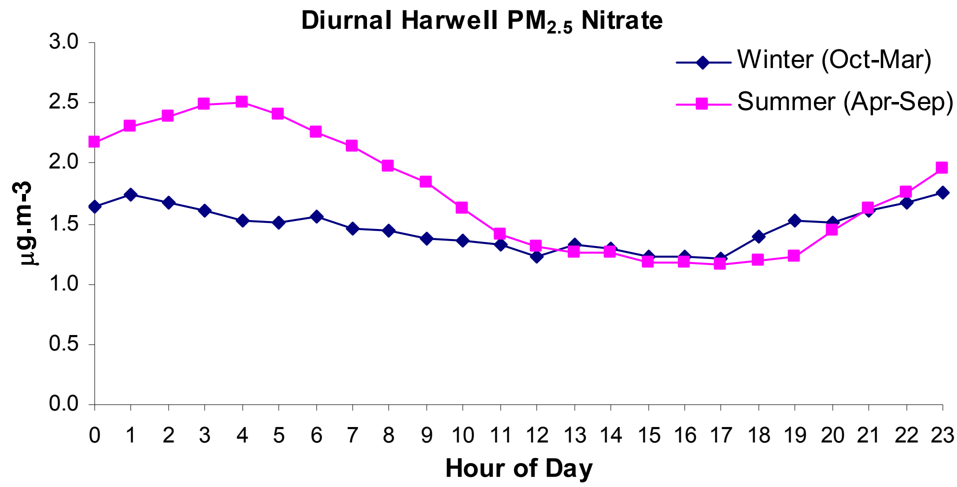


Figure 10b. Diurnal representation of Harwell Nitrate 2006

Figure 10b also shows the influence of temperature on the reported nitrate results - the hottest time of the day, the afternoon, has the lowest nitrate concentration. This is more pronounced during the summer months.

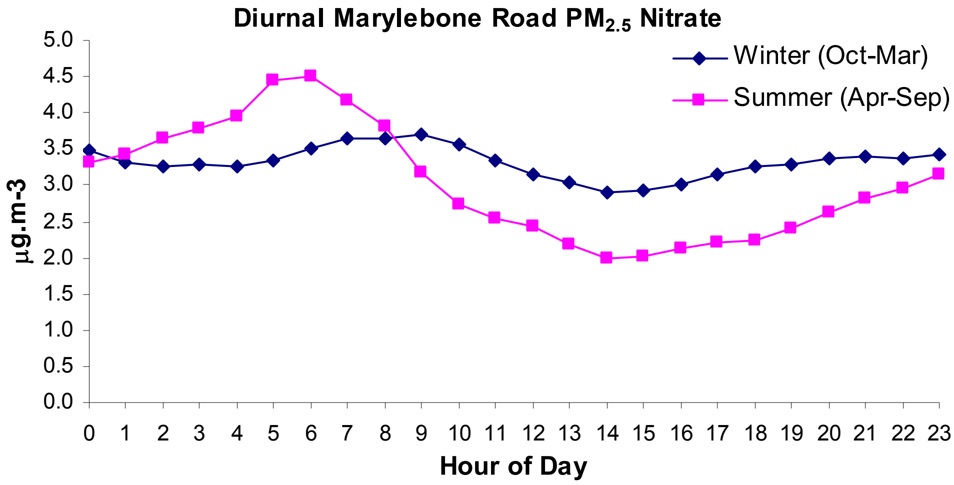


Figure 10c. Diurnal representation of Marylebone Road Nitrate 2006

At Marylebone Road the afternoon also has the lowest nitrate concentrations, for the same reasons. Again, this is more pronounced during the summer months.

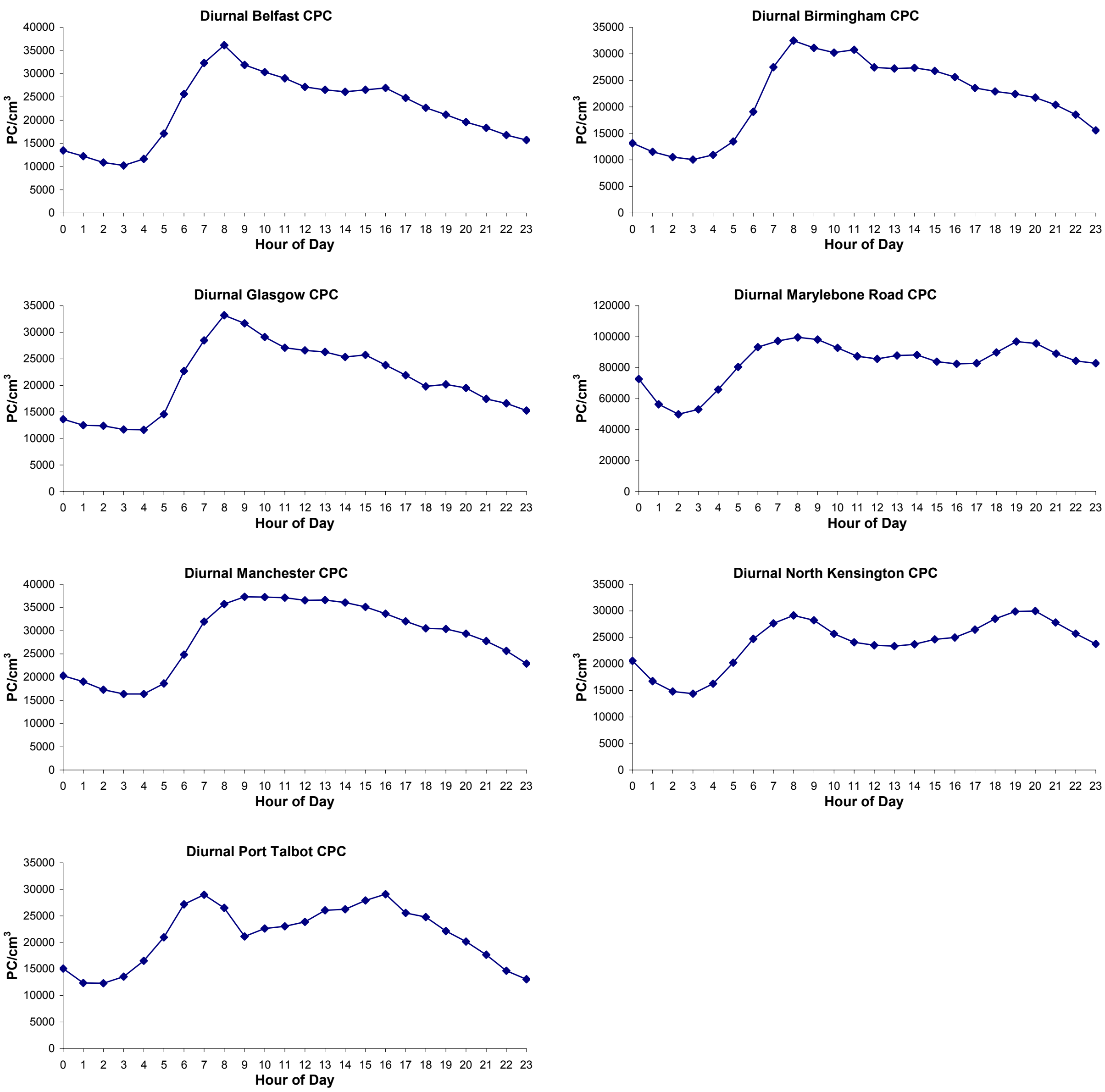
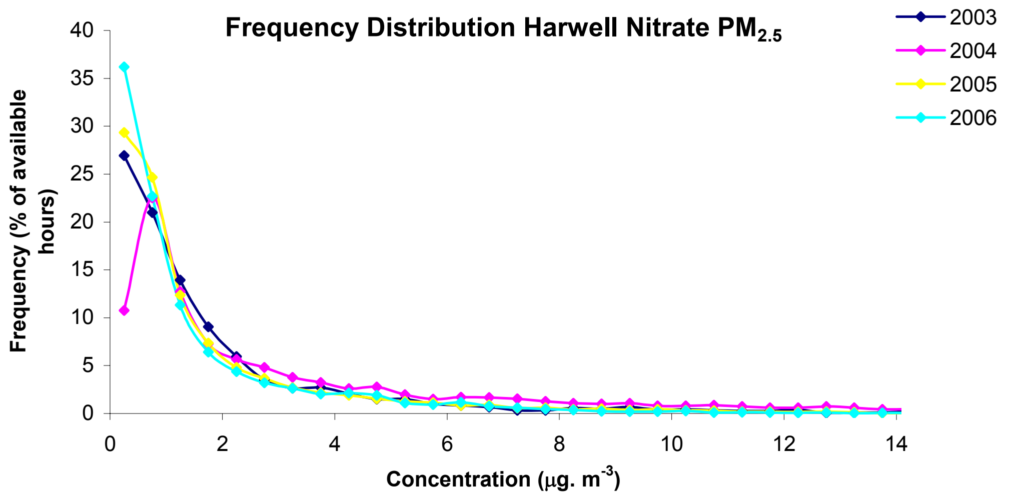


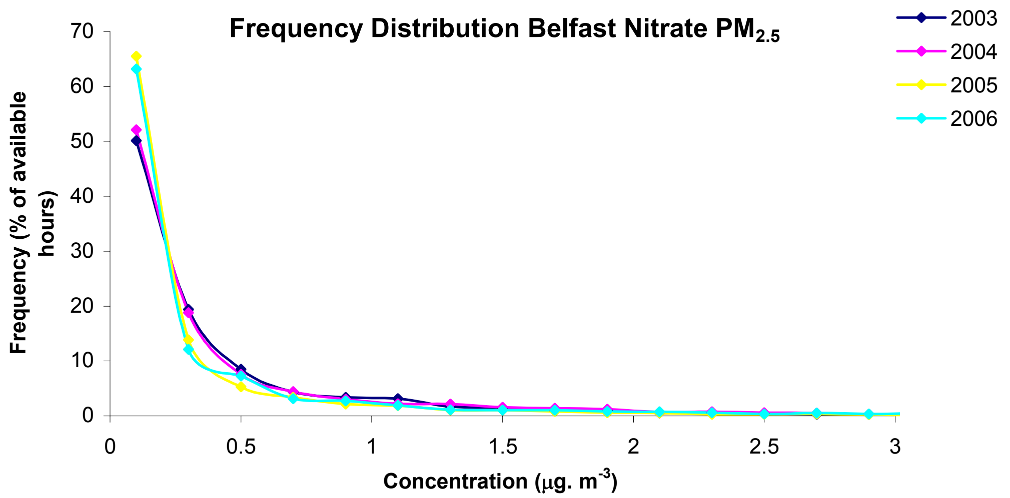
Figure 10d. Diurnal representation of all CPCs 2006

These graphs highlight the average particle count for each hour of the day. All sites show a peak at about 8am, the morning rush hour. Some sites (Port Talbot, Marylebone Road and North Kensington) also show a similar peak for the afternoon/evening rush hour (it is slightly later at the London sites). The peaks at Marylebone Road are less pronounced because the traffic levels are high throughout the day. Counts are lowest at all sites between midnight and about 4am.

Frequency Distributions

The following frequency distributions are intended to compare the data of 2006 with the previous years' data.





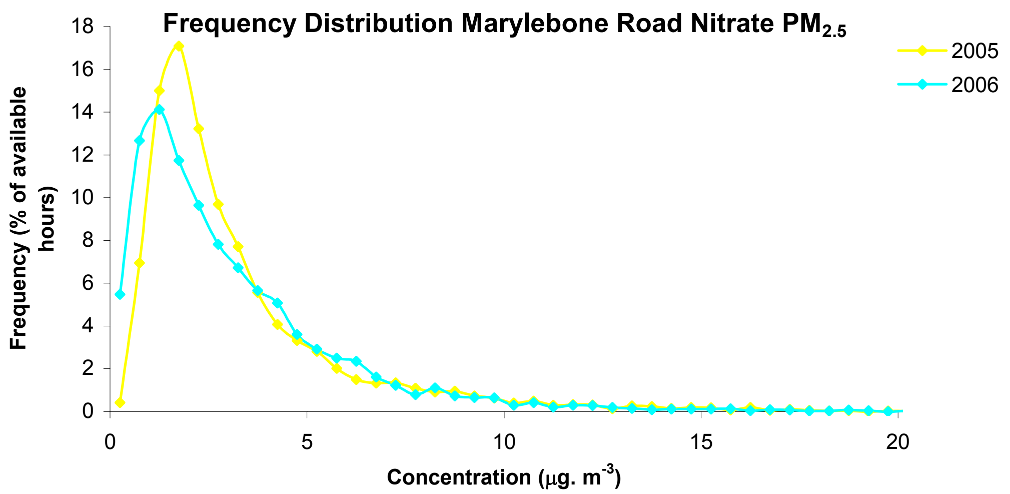


Figure 11a. Automatic nitrate concentration frequency distributions

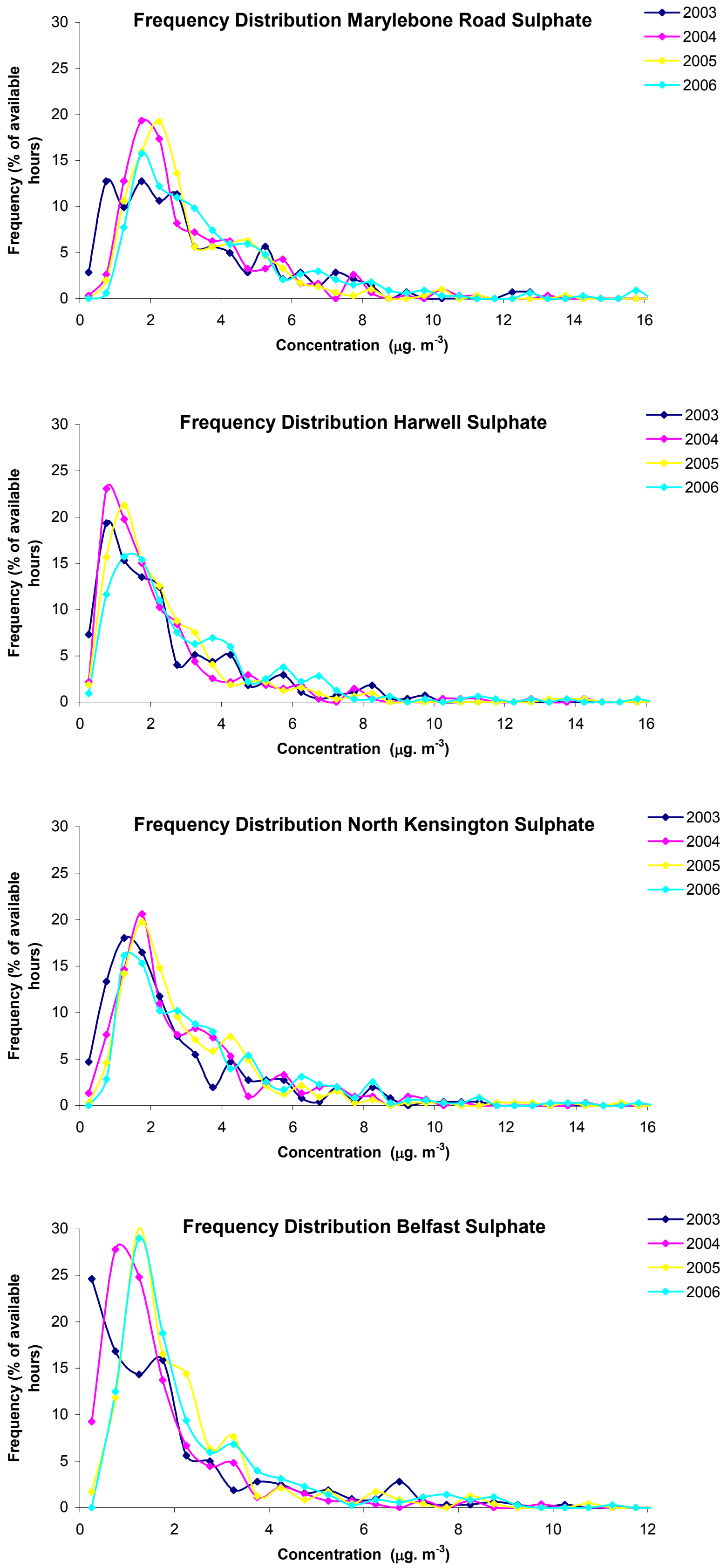


Figure 11b. Daily sulphate concentration frequency distributions

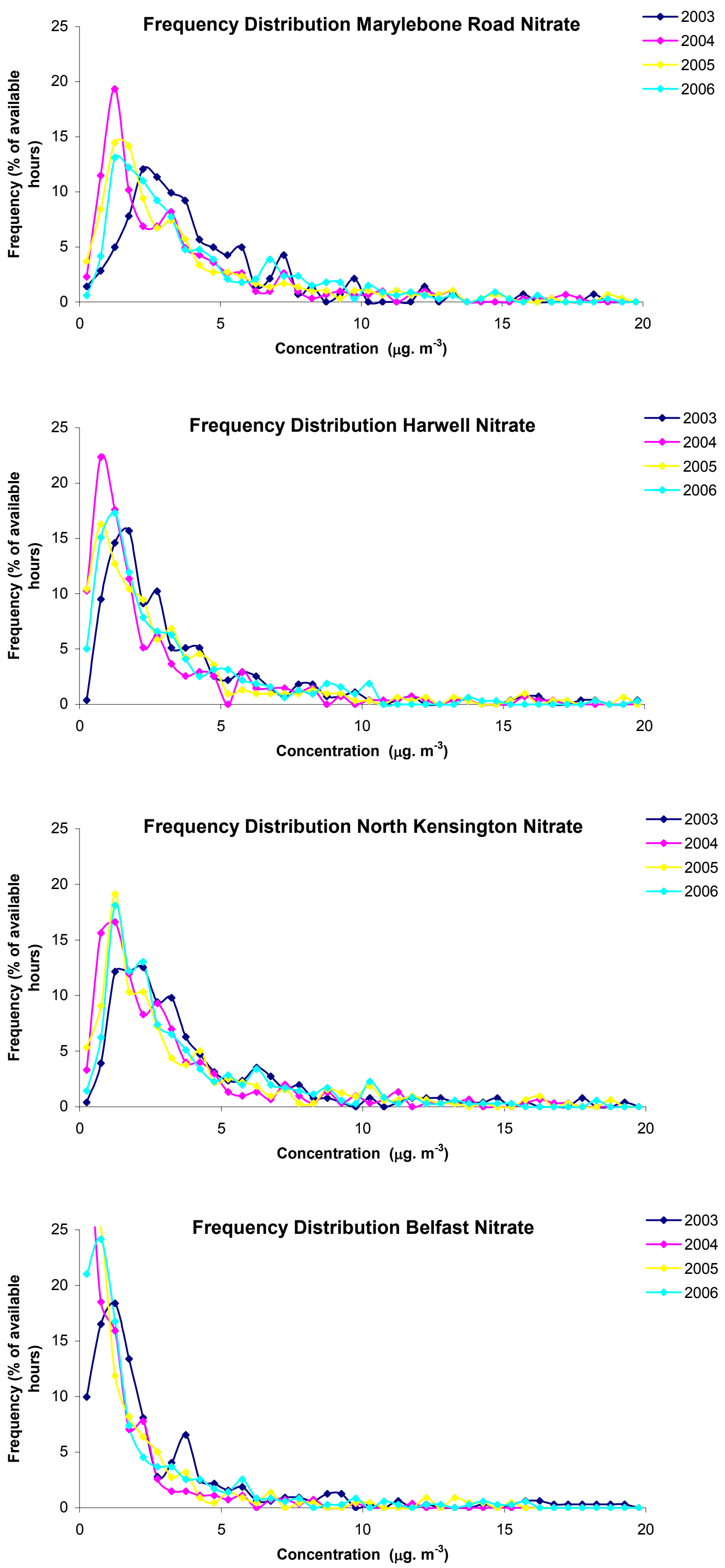


Figure 11c. Daily nitrate concentration frequency distributions

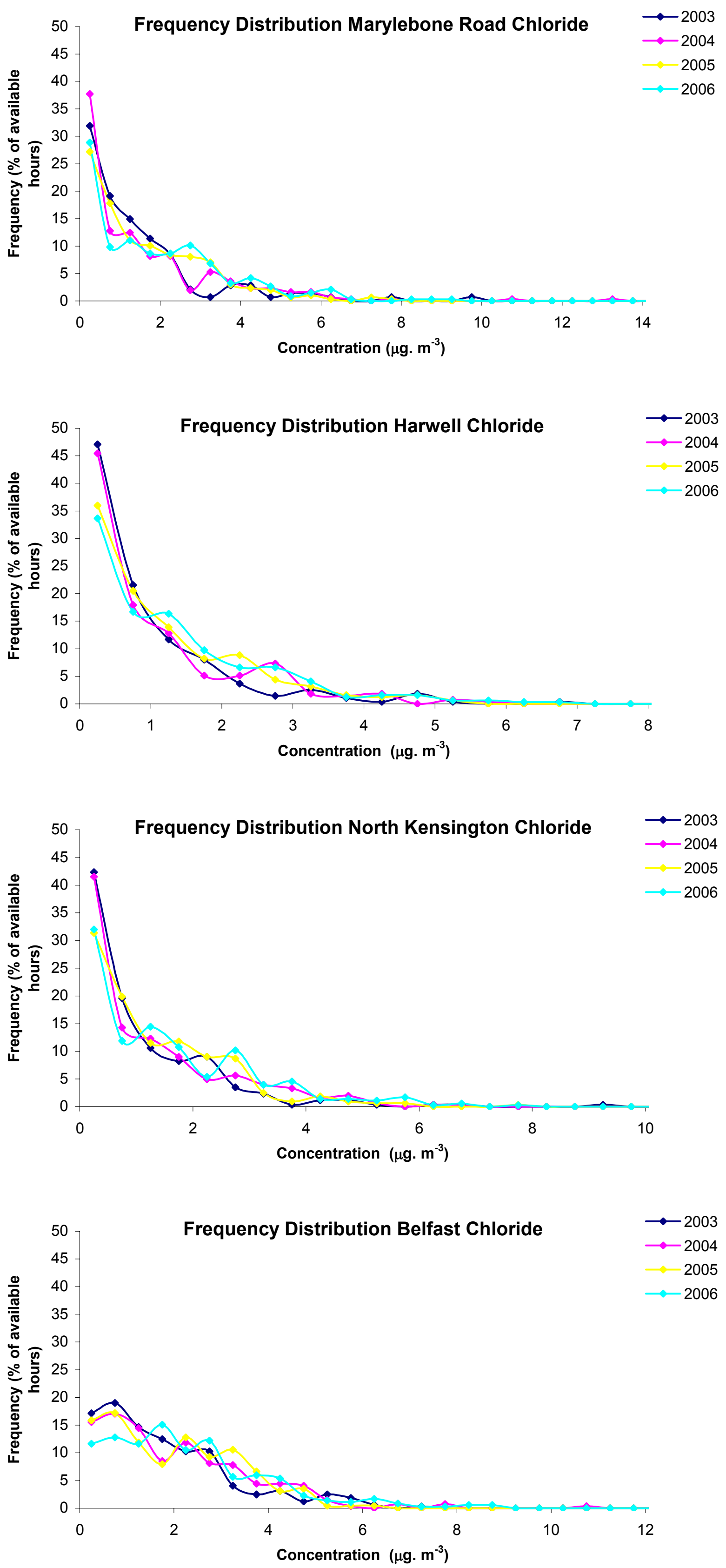


Figure 11d. Daily chloride concentration frequency distributions

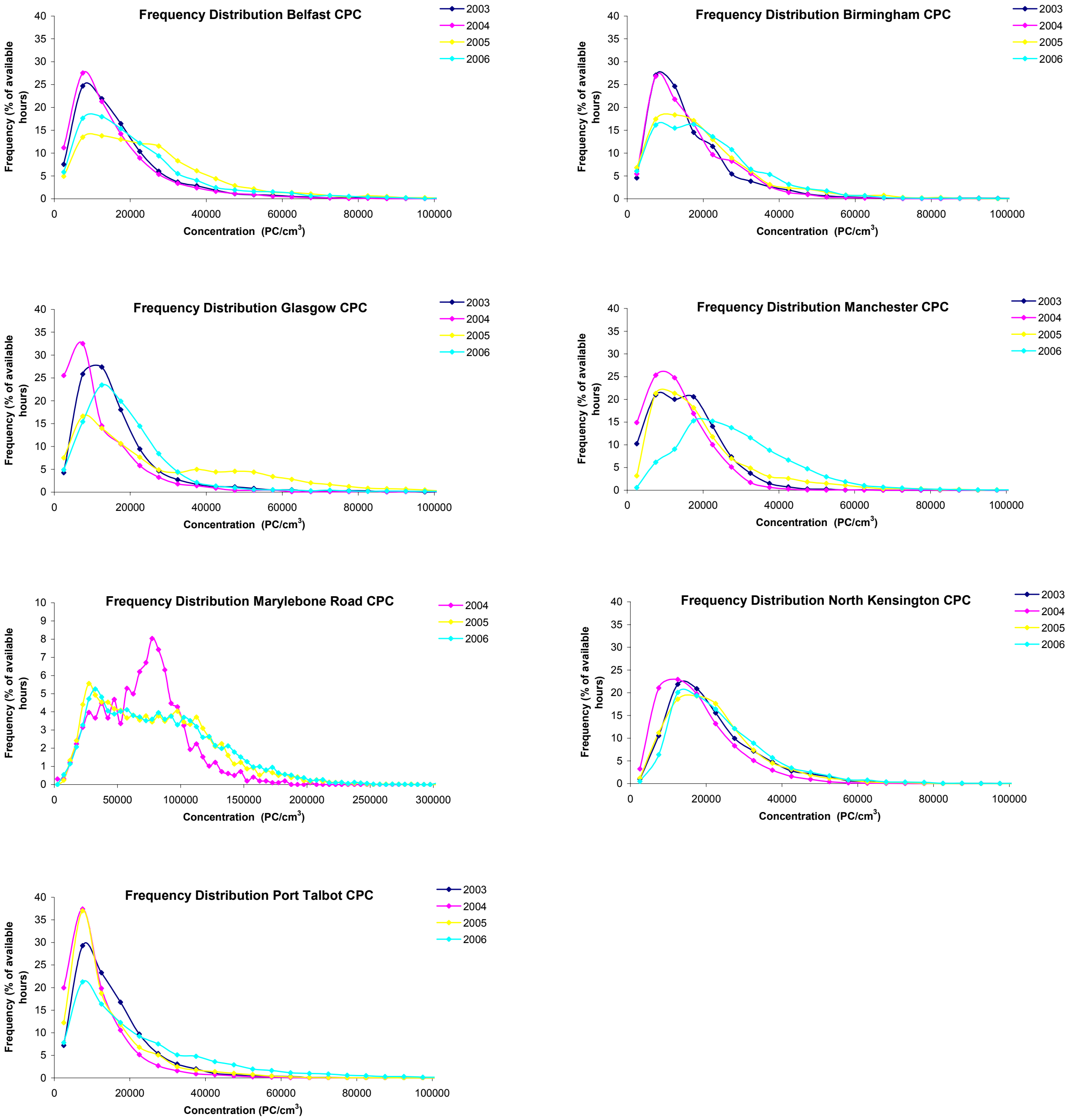


Figure 11e. CPC frequency distributions at all sites

For the majority of sites, over time the most frequent concentration peak is becoming broader and moving towards higher values, because the concentrations of particles are increasing (as demonstrated by Figure 9d). This is particularly clear in the Manchester frequency distribution. It is also worth noting that the shape of the Marylebone Road frequency distribution is very different in 2004 compared to 2005 and 2006. Although the CPC was only installed part way through 2004 at Marylebone Road, this is not thought to be the reason for the difference. However, Table 11 and Figure 9d both suggest that 2004 was a year with unusually low particle counts.

Wider Context Update

Other relevant UK Networks

The measurements made within this Network are one research resource in the area of particulate matter. Other sources of data should be borne in mind.

EMEP sites:

The Cooperative Programme For Monitoring And Evaluation Of The Long-Range Transmission Of Air Pollutants In Europe (EMEP) is setting up a Network of monitoring sites across Europe making detailed measurements of PM composition at background locations including Auchencorth Moss and Harwell.

The instrumentation relevant to this Network will include:

- A MARGA Steam Jet Aerosol Collector, measuring PM_{10} and $PM_{2.5}$ sulphate, nitrate, ammonium, sodium, potassium, calcium and magnesium ions, hourly.

- OC/EC by aethalometry, with supplementary analysis of filter samples.

AURN measurements:

Any investigation of PM must be linked to the officially reported PM_{10} and $PM_{2.5}$ measurements. The discrepancies between the reference gravimetric method and the standard TEOM instrument are well known, and it is also becoming more apparent that the reference method needs to be very carefully implemented to produce reliable results. Results from this network will help to resolve practical questions such as the validity of the KCL Volatile Correction Model, which uses regional FDMS data to correct local TEOM data.

Black Smoke measurements:

There are currently 21 sites that make daily Black Smoke measurements using the reflectance of filter samples. Although the conventional Black Smoke index (given in units of $\mu g/m^3$) is quite different from a measure of elemental carbon, NPL is investigating the possibility that alternative processing of the reflectance data can give a more reliable EC indicator.

Ammonia and Acid Deposition Monitoring Networks:

Daily measurements of sulphate, and monthly measurements of nitrate, chloride and ammonium are made at rural sites through these Networks. The sites have been rationalised during 2006. The data has not been available for comparison during the writing of this report.

EMEP PM Report

EMEP has recently drafted their EMEP Particulate Matter Assessment Report (Second Draft March 2007). Their conclusions can be summarised from statements such as “There is still a great lack of understanding of some of the major PM components” and “Current knowledge on PM levels and speciation are hampered by shortcomings in monitoring and modelling. Measurements of PM mass concentrations may not necessarily be comparable across Europe because of the comparability of the different methods, because of differences in correction factors applied to the measurements to make them comparable with reference methods and because of a number of specific analytical issues that may hamper the comparison of PM composition measurements.”

Proposal for revised EU Air Quality Directive

The proposal, released as an Advanced Preliminary Version as COM(2005) 447 on 21 September 2005, aims to revise and combine the Framework Directive 96/62/EC, the first three “Daughter” Directives, covering sulphur dioxide, NO_x, PM, lead, benzene, carbon dioxide and ozone, and the “Exchange of Information Decision”.

Three aspects are relevant to this Network. Firstly, the existing PM legislation is based on control of PM_{10}, while the Proposal moves the emphasis to $PM_{2.5}$. Research-led measurements such as those on this Network should therefore make due emphasis on the $PM_{2.5}$ fraction. Secondly, there is more explicit allowance for pollution arising from “natural sources” to be disregarded. Again, research-led measurements should make the determination of the “natural” fraction of PM a clear aim.

Lastly, Annex IV includes the statement “Measurement of $PM_{2.5}$ must include at least the mass concentration and appropriate compounds to characterise its chemical composition. At least the list of chemical species below shall be included.”

SO_4^{2-}	Na^+	NH_4^+	Ca^{2+}	Elemental carbon (EC)
NO_3^-	K^+	Cl^-	Mg^{2+}	Organic carbon (OC)

Many of these components are those currently measured by this Network. There is a need to clarify what is meant in practice by EC and OC.

The current situation is that the Council reached political agreement on 23 October 2006. The text will be adopted as a common position at a forthcoming session of the Council and sent to the European Parliament with a view to the second reading. The agreement confirmed essentially the general approach reached on 27 June 2006, that already included the following relevant changes:

(a) a non-binding target value for $PM_{2.5}$ in 2010 to be replaced by a binding limit value in 2015 (25µg/m^3 for both target value and limit value);
(b) the possibility to postpone attainment of the limit value for PM_{10} until three years after entry into force of this Directive;
(c) the principle that limit values should apply everywhere, but in certain locations compliance with limit values should not be assessed.

CEN standards

CEN TC 264 WG 15 is in the process of updating the gravimetric PM_{10} standard EN 12341:1998. One aim is to tighten the specifications for filter handling and transport in line with the EN 14907 standard for $PM_{2.5}$. The main outstanding issues are the specifications for "reference" filter material, and the humidity level during weighing.

The working group is also in the early stages of drafting a CEN standard for automatic PM_{10} measurement. There are no CEN standards planned for ambient particle number, size, or composition.

ISO standards

There are many standards for particle sizing being prepared within ISO TC24 SC4, though they are mainly not applicable to measuring particles in air. The most relevant is ISO/WD 15900 "Determination of Particle Size Distribution – Differential Electrical Mobility Analysis for Aerosol Particles" – i.e. measurements using SMPS. This is near to completion.

This standard does not include requirements for calibrating the number concentration part of the measurement – i.e. CPCs. This will form the topic of a new standard (ISO 27891).

EUSAAR recommendation for SMPS measurements

The EUSAAR project (European Super-sites for Atmospheric Aerosol Research) includes 20 sites across Europe including Harwell. It has recommended that SMPS instruments should standardise the aerosol size distribution by measuring under dry conditions (<30% RH).

- The aerosol flow should be dried (for example using a naphion drier). Losses in the drier should be calibrated;

- The sheath air flow should be dried (for example using a naphion drier or an aerosol diffusion dryer);

- The RH of the aerosol flow should be monitored by a calibrated humidity sensor (with an accuracy higher than 5% of RH).

The implications for these changes at Harwell and other sites are being considered.

Instrumentation Update

The current options for composition measurement instruments are given below:

Reference (non-automatic) methods:

Nitrate and Sulphate	Filter sampling (e.g. using Partisol) followed by Ion Chromatography (IC)
OC/EC	Sunset Labs or DRI Model 2001 – filter sampling followed by combustion, methanisation then flame ionisation detection (FID)

Automatic (hourly) measurements:

Nitrate	R&P 8400N – combustion then NO_2 measurement – to be discontinued from 1 March 2008
	URG 9000A (ET) or Marga (SJAC) – solution of particles then automated IC
Sulphate	R&P 8400S – now discontinued
	Thermo Electron 5020 – combustion then uv fluorescence
	URG 9000A (ET) or Marga (SJAC) – solution of particles then automated IC
OC/EC	R&P 5400 – combustion to CO_2 then NDIR – to be discontinued from 1 March 2008
	Sunset Labs - combustion to CO_2 then NDIR, with pyrolysis correction

VAM Update

NPL is funded by DTI, via the Valid Analytical Measurement (VAM) programme within the National Measurement System, to carry out research and provide measurement services and facilities for various types of analysis including gas and particulate analysis. Within VAM Projects P1 and P2, the work on ambient particle analysis has recently been expanded and aligned to provide support for many of the measurements within this Network.

The work is in two broad areas. Firstly, a laboratory facility has been developed, providing the means to generate, manipulate, detect and characterise a wide range of nanoparticles in the size range 1 to 500 nanometres. The equipment installed includes particle generators for primary soot, salt and organic nanoparticles with a range of size distributions, and detectors that can detect both electrically charged and neutral particles over a concentration range of several orders of magnitude, including CPC and SMPS instruments. This work is aimed at quantifying instrumental issues in a laboratory environment, and determining the suitability of different instruments for different tasks.

Secondly, a field monitoring site for research purposes has been established in a dedicated climate controlled cabin, with the aim of carrying out short and medium term comparative trials in ambient air. This will be used for particle counting and sizing, particle mass, and particle composition measurements. It is intended to compare spare Network instruments with a range of other instruments and reference methods. In the case of particle composition, NPL has a Dionex Ion Chromatography instrument for reference analysis of filter samples, and a Sunset Labs instrument for "reference" analysis of OC/EC.

Topic Reports and Publications

Reports and papers produced or published since the start of the contract include:

CPEA 28: Airborne Particulate Concentrations and Numbers in the UK (phase 2). State of Network Report, NPL Report DQL-AS 019, September 2005

CPEA 28: Airborne Particulate Concentrations and Numbers in the UK (phase 2). Strategic Network Review, NPL Report DQL-AS 020, November 2005

CPEA 28: Airborne Particulate Concentrations and Numbers in the UK (phase 2). Annual Report 2005, NPL Report DQL-AS 028, Revised July 2006

CPEA 28: Airborne Particulate Concentrations and Numbers in the UK (phase 2). Annual Audit Report, NPL Report DQL-AS 031, July 2006

Comparison of Methods for Organic and Elemental Carbon PM10 Concentrations at Marylebone Road for the Period 07/09/06 to 31/12/06, NPL Report DQL-AS 035, February 2007

CPEA 28: Airborne Particulate Concentrations and Numbers in the UK (phase 2). Estimation of Measurement Uncertainty in Network Data, NPL Report DQL-AS 037, March 2007

Multisite Study of Particle Number Concentrations in Urban Air, R.M. Harrison and A.M. Jones, Environ. Sci. Technol., 39, 6063-6070 (2005).

The Use of Trajectory Cluster Analysis to Examine the Long-Range Transport of Secondary Inorganic Aerosol in the UK, S.S. Abdalmogith and R.M. Harrison, Atmos. Environ., 39, 6686-6695 (2005).

Interpretation of Particulate Elemental and Organic Carbon Concentrations at Rural, Urban and Kerbside Sites, A.M. Jones and R.M. Harrison, Atmos. Environ., 39, 7114-7126 (2005).

Fine (PM2.5) and Coarse (PM2.5-10) Particulate Matter on a Heavily Trafficked London Highway: Sources and Processes, A. Charron and R.M. Harrison, Environ. Sci. & Technol., 39, 7768-7776 (2005).

An Analysis of Spatial and Temporal Properties of Daily Sulphate, Nitrate and Chloride Concentrations at UK Urban and Rural Sites, S.S. Abdalmogith and R.M. Harrison, J. Environ. Monit., 8, 691-699 (2006).

Particulate Sulphate and Nitrate in Southern England and Northern Ireland during 2002/3 and its Formation in a Photochemical Trajectory Model, S.S. Abdalmogith, R.M. Harrison and R.G. Derwent, Sci. Tot. Environ., 368, 769-780 (2006).

Intercomparison of Secondary Inorganic Aerosol Concentrations in the UK with Predictions of the Unified Danish Eulerian Model, S.S. Abdalmogith, R.M. Harrison and Z. Zlatev, J. of Atmos. Chem., 54, 43-66 (2006).

Estimation of the Emission Factors of Particle Number and Mass Fractions from Traffic at a Site Where Mean Vehicle Speeds Vary Over Short Distances, A.M. Jones and R.M. Harrison, Atmos. Environ., 40, 7125-7137 (2006).

Assessment of Natural Components of PM10 at UK Urban and Rural Sites, A.M. Jones and R.M. Harrison, Atmos. Environ., 40, 7733-7741 (2006).

What are the Sources and Conditions Responsible for Exceedences of the 24 h PM_{10} Limit Value (50 µg m^{-3}) at a heavily trafficked London site?, A. Charron, R.M. Harrison and P.G. Quincey, Atmos. Environ., 41, 1960-1975 (2007).

Annex 1. Network Instruments

Site	Type	Hourly $PM_{2.5}$ nitrate	Hourly PM_{10} OC/EC	Daily PM_{10} filter (anions)	CPC	SMPS
Belfast Centre	Urban centre	x	x	x	x	
Birmingham Centre	Urban centre				x	
Glasgow Centre	Urban centre				x	
Harwell	Rural	x	x	x		x
London Bloomsbury	Urban centre					x
London Kensington	Urban background		x	x	x	
London Marylebone Road	Kerbside	x	x	x	x	x
Manchester Piccadilly	Urban centre				x	
Port Talbot	Urban background				x	

Spare Equipment: 1 hourly OC/EC; 2 hourly nitrate; 1 hourly sulphate; 1 CPC

Equipment models:

CPC	TSI model 3022A
Hourly nitrate	Thermo 8400N
Hourly carbon	Thermo 5400
Hourly sulphate	Thermo 8400S
Daily sulphate	Thermo Partisol 2025
SMPS	TSI model 3071 (to March 06)

Annex 2. Map of Current Network Sites

Annex 3. Estimation of Measurement Uncertainty in Network Data

This text reproduces the Executive Summary from the NPL report DQL-AS 037, on estimation of measurement uncertainty:

This NPL Report is an introduction to the measurement uncertainties associated with data produced by the Airborne Particulate Concentrations and Numbers Network.

The audit and calibration of the network instruments provides correction factors required to eliminate bias from the measurement results. These are applied during the data ratification process. The tests conducted during the audits, and during routine testing of the instruments, also allow an estimation of the random uncertainty in the measurement process. Further investigation may be required to reliably quantify the uncertainties in these data.

For each model of instrument on the Network the uncertainty associated with the measurement, *relative to other similar instruments*, has been estimated. Note that the term 'uncertainty' is usually applied in a broader sense, as described in the Introduction.

- The results produced by the CPCs are strongly dependent on the low size cut-off point, which varies between models, making it impossible to directly compare different models. There are two modes of detection (single particle and photometric) that are commonly used during Network operation, and therefore two uncertainty estimations. The greatest contributions to uncertainty are detector drift and calibration. Switching between detection modes also has some measurement issues.

- The automatic nitrate analyser is a more complicated instrument, which relies on a series of assumptions and conversion factors. It is calibrated several times a year, but detector drift between calibrations is a large contribution to the overall uncertainty, as are converter and collection efficiencies.

- When functioning correctly, the main problem with the automatic carbon instruments is that the measurand is different to manual (reference) methods for OC/EC. However, the estimation of uncertainty given in this report is for a fully functioning instrument, compared to another of the same type.

- Daily nitrate, sulphate and chloride filters are analysed manually in a laboratory and the uncertainty in the analytical results is low due to strict QA/QC procedures. However, due to the method of sample collection, particle-laden filters can be exposed to ambient temperatures and gases for up to two weeks. During this time, it is possible that some volatile species are removed from the filter, and that some species are involved in chemical reactions with ambient gases, so that sampling and storage uncertainties can be significant.

- SMPS uncertainties have not been estimated because the instruments are currently being replaced with a different model. Their uncertainty will be addressed at a later date.

Annex 4. Comparison of Methods for Organic and Elemental Carbon PM_{10} Concentrations at Marylebone Road

This text reproduces the Executive Summary from NPL report DQL-AS 035, on organic and elemental carbon at Marylebone Road:

This Report was prepared by NPL as part of the 2005-2007 UK Airborne Particulate Concentrations and Numbers Monitoring contract with the Department for the Environment, Food and Rural Affairs.

The report summarises the results of parallel measurements of the organic and elemental (OC/EC) carbon content of PM_{10} suspended particulate matter at Marylebone Road during the period 07/09/06 to 31/12/06. Measurements were made using the Sunset Laboratory Carbon Aerosol Analysis Lab Instrument and the automatic Thermo Electron Corporation Series 5400 Ambient Carbon Particulate Monitor.

The aim of the intercomparison was to see if the automatic (Thermo) instrument gave similar values to the manual Sunset instrument, which follows a method similar to the US reference method. There is no European reference method for these measurements. A US EPA study in December 05 showed that the automatic method gave poor agreement with the manual reference method for elemental carbon.

The study will inform the interpretation of results from the Network, which currently includes four Thermo instruments, and also strategy for monitoring OC/EC by the Network in the future.

The results of the intercomparison showed that that the manual method reported organic carbon concentrations similar to the automatic method, while it reported elemental carbon concentrations between three and four times the magnitude of the automatic method. When adding the organic and elemental concentrations to form a measure of total carbon, the manual method reported approximately two times the concentration of the automatic method. The measurements produced by the manual method are in agreement with previous measurements reported by the Air Quality Expert Group in the UK.

Further work is to be carried out at an urban background site to show whether these results are applicable to other site locations.

Annex 5. Instrument Repairs

Site	Instrument	Callout Date	Final Repair Date	Fault
Belfast	Carbon	14/06/2006	20/06/2006	Fuses replaced, lamps replaced
		25/07/2006	17/08/2006	Collectors replaced and sample pump rebuilt
		04/10/2006	18/10/2006	CO2 pump fitted
		04/10/2006	08/11/2006	Pinch valves rebuilt
Belfast	Nitrate	31/05/2006	20/06/2006	Dryer element removed and instrument and pump shut down
		21/09/2006	03/10/2006	Leak repaired
		31/10/2006	08/11/2006	Analyser flow calibrated, NOx analyser zero and span calibrated
Harwell	Carbon	24/02/2006	26/02/2006	Collectors cleaned
		12/06/2006	12/06/2006	Replaced faulty CO2 pump
		06/09/2006	08/09/2006	Recalibrated the flow sensor and analyser re-commissioned
		18/09/2006	18/09/2006	Flow calibrated and service clean performed
		04/10/2006	20/10/2006	Flow sensor changed, main flows calibrated, CO2 sensor flow calibrated
		28/10/2006	07/11/2006	Pinch valve removed and rebuilt
		14/11/2006	15/11/2006	Instrument in CLEAN mode. Instrument re-set
		04/12/2006	12/12/2006	Instrument reconfigured and calibrated remotely
Harwell	Nitrate	06/09/2006	08/09/2006	CPU board damaged. Returned to workshop.
		23/10/2006	24/10/2006	Removed nitrate NOx analyser and replaced with hot spare, system leak tested and calibrated, back up battery replaced on CPU board
		07/11/2006	07/11/2006	Pulse generator replaced
		13/11/2006	22/12/2006	Temperature probe replaced. Instrument recalibrated.
Harwell	Partisol	02/05/2006	02/05/2006	Temperature sensors recalibrated
		28/10/2006	07/11/2006	RS232 cable replaced

Site	Instrument	Callout Date	Final Repair Date	Fault
North Kensington	Carbon	27/01/2006	27/01/2006	Replaced CPU board on CO2 analyser
		05/02/2006	05/02/2006	Adjusted sensor for the mains voltage
		01/03/2006	20/03/2006	Instrument replaced with spare
		25/04/2006	25/04/2006	New lamps and 4amp fuse was replaced
		08/06/2006	19/06/2006	Replaced circulating pump.
		10/07/2006	18/07/2006	Leak repaired
		18/09/2006	18/09/2006	Remote service clean
		25/09/2006	28/09/2006	Collectors replaced
		27/10/2006	02/11/2006	Lamps replaced
Marylebone Road	Carbon	16/08/2006	29/08/2006	Changed LICOR CO2 Analyser
		18/09/2006	20/09/2006	Lamps replaced, temperatures and flows calibrated
Marylebone Road	Nitrate	02/03/2006	02/03/2006	Replaced with hot spare
		20/03/2006	20/03/2006	Analyser cell replaced
		10/08/2006	13/08/2006	Changed purge generator, re-connected ambient temperature sensor, re-calibrated NOx analyser
		16/08/2006	24/08/2006	RS232 comms board replaced
		04/12/2006	27/12/2006	Humidity sensor replaced

References

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[iv] *Comparison of Methods for Organic and Elemental Carbon PM10 Concentrations at Marylebone Road for the Period 07/09/06 to 31/12/06,* NPL Report DQL-AS 035, February 2007

[v] *Comparison of Integrated Filter and Semi-Continuous Measurements of PM2.5 Nitrate, Sulfate, and Carbon Aerosols in the Speciation Trends Network (STN),* US Environmental Protection Agency EPA 454/R-05-004, 2005

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